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(21) International Application Number: PCT/GB99/00246 (22) International Filing Date: 10 February 1999 (10.02.99) (30) Priority Data: 9802852.5 11 February 1998 (11.02.98) GB (71) Applicant (for all designated States except US): BRITISH NUCLEAR FUELS PLC [GB/GB]; Risley, Warrington, Cheshire WA3 6AS (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): THIED, Robert, Charles [GB/GB]; British Nuclear Fuels plc, Research & Technology, Sellafield, Seascale, Cumbria CA20 1PG (GB). SEDDON, Kenneth, Richard [GB/GB]; The Queens University, School of Chemistry, Stranmillis Road, Belfast BT9 5AG (GB). PITNER, William, Robert [US/GB]; The Queens University, School of Chemistry, Stranmillis Road, Belfast BT9 5AG (GB). ROONEY, David, William [IE/GB]; The Queens University, School of Chemistry, Stranmillis Road, Belfast BT9 5AG (GB). (74) Agent: HARRISON GODDARD FOOTE; Belmont House, 20 Wood Lane, Leeds LS6 2AE (GB).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: NUCLEAR FUEL REPROCESSING (57) Abstract There is described a method for treating or reprocessing spent nuclear fuel to substantially separate fissile material from fission products which comprises dissolving the spent fuel or constituent parts of the spent fuel in an ionic liquid and in particular to recover uranium and/or plutonium. There is also described a novel crystal structure.		

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NUCLEAR FUEL REPROCESSING

The present invention relates to the treating or reprocessing of nuclear fuel using ionic liquids and to a novel form of a uranium compound.

5

Most commercial nuclear fuel reprocessing plants use the Purex process, in which the spent fuel is dissolved in nitric acid and the dissolved uranium and plutonium are subsequently extracted from the nitric acid solution into an organic phase of tributyl phosphate (TBP) dissolved in an inert hydrocarbon such as odourless kerosene. The organic phase is then subjected to solvent extraction techniques to partition the uranium from the plutonium. The Purex process involves a number of difficulties and is subject to continuous research and development activities to ameliorate these problems.

15 Internationally there are also two well developed processes which use molten salts for the reprocessing/waste conditioning of irradiated nuclear fuel. The Argonne National Laboratory electrometallurgical treatment process (ANL – EMT) and the Dimitrovgrad SSC – RIAR process both use molten salts at high temperatures (773 and 1000K, respectively). The ANL process is fundamentally electrorefining technology, using current flow to ensure the oxidation of a uranium anode to form uranium ions in the molten salt electrolyte. At the cathode the uranium is reduced and electrodeposited as uranium metal. The SSC – RIAR process uses chemical oxidants (chlorine and oxygen gases) to react with powdered UO_2 fuel to form higher oxidation state compounds such as UO_2Cl_2 which are soluble in the molten salt. At the cathode the uranium compounds are reduced to UO_2 which forms a dendrite deposit.

25

Molten salts have been proposed for use in the reprocessing of irradiated fuels from Light Water Reactors (LWRs). These molten salts are typically mixtures of salts which are liquid only at high temperatures and this causes inherent disadvantages in a reprocessing plant.

30

Ionic liquids free of molecular solvents were first disclosed by Hurley and Wier in a series of US patents (24446331, 2446339, 2446350). These ionic liquids comprised

- aluminium(III) chloride and a variety of N-alkylpyridium halides, and afforded a conducting bath for aluminium electroplating. In general terms an ionic liquid is a salt, a mixture of salts, or a mixture of components which produce a salt or salts, which melts below or just above room temperature (in terms of this invention, a salt consists entirely
5 of cationic and anionic species). The term "ionic liquid" relates to a salt, a mixture of salts, or a mixture of components which produce a salt or salts, and which melts at a temperature up to 100°C eg from -50 to 100°C. The cation in these ionic liquids is usually organic.
- 10 Traditionally molten salts melt above 150°C, and more frequently at much higher temperatures than this. Such salts are usually composed of inorganic cations, and are only suitable for high temperature processes. There is therefore novelty in the application of ionic liquids to fuel reprocessing.
- 15 Known ionic liquids include aluminium(III) chloride in combination with an imidazolium halide, a pyridinium halide or a phosphonium halide. Examples of the halides include 1-ethyl-3-methylimidazolium chloride, *N*-butylpyridinium chloride and tetrabutylphosphonium chloride. An example of a known ionic liquid system is a mixture of 1-ethyl-3-methylimidazolium chloride and aluminium(III) chloride.
- 20 E. S. Lane, J. Chem. Soc. (1953), 1172-1175 describes the preparation of certain alkylpyridinium nitrate ionic liquids, including sec-butylpyridinium nitrate. No use of the liquids is mentioned but reference is made to the pharmacological activity of decamethylenebis(pyridinium nitrate).
- 25 L. Heerman et al., J. Electroanal. Chem., 193, 289 (1985) describe the dissolution of UO_3 in a system comprising *N*-butylpyridinium chloride and aluminium(III) chloride.
- 30 K. R. Seddon, J. Chem. Tech. Biotechnol. 1997, **68**, 351-356 discusses the design principles for room-temperature ionic liquids, some of their properties and the rationale for using these solvents.

International Patent Application WO 96/32729 teaches that oxide nuclear fuels may be dissolved in a fused alkali metal carbonate to produce a compound which may be further processed so as to extract uranium therefrom.

- 5 International Patent Applications WO 95/21871, WO 95/21872 and WO 95/21806 relate to ionic liquids and their use to catalyse hydrocarbon conversion reactions (e.g. polymerisation or oligomerisation of olefins) and alkylation reactions. The ionic liquids are preferably 1-(C₁-C₄ alkyl)-3-(C₆-C₃₀ alkyl) imidazolium chlorides and especially 1-methyl-3-C₁₀ alkyl-imidazolium chloride, or 1-hydrocarbylpyridinium halides, where the
10 hydrocarbyl group is for example ethyl, butyl or other alkyl.

- International Patent Application No PCT/GB97/02057 (WO 98/06106) describes a method of dissolving in an ionic liquid a metal in an initial oxidation state below its maximum oxidation state, wherein the ionic liquid reacts with the metal and oxidises it to
15 a higher oxidation state. The initial metal may be in the form of a compound thereof and may be irradiated nuclear fuel comprising UO₂ and/or PuO₂ as well as fission products. Typically the ionic liquid is nitrate-based, for example a pyridinium or substituted imidazolium nitrate, and may contain a Brønsted or Franklin acid. Suitable acids are HNO₃, H₂SO₄ and [NO⁺]. This International Patent application also describes certain
20 novel ionic liquids, including 1-butylpyridinium nitrate, 1-octylpyridinium nitrate, other nitrate-based ionic liquids whose cation component is not exclusively alkylpyridinium or polymethylenebis (pyridinium), and substituted imidazolium nitrates, especially 1-butyl-3-methylimidazolium nitrate, 1-hexyl-3-methylimidazolium nitrate and 1-octyl-3-methylimidazolium nitrate.

25

- Specifically, the oxidising ionic liquids described in WO 98/06106 may i) be intrinsically oxidising, ii) have an oxidising agent added, and/or iii) have a promoting agent of oxidising ability added. The agents may be an oxidant dissolved in a non-oxidising liquid or an auxiliary agent to increase the oxidising reactivity of another oxidising species. If
30 the solvent contains nitrate ions, the agent increases the oxidising reactivity of the medium beyond that which would be provided by the nitrate ions themselves; as described above, such agents include acids and particularly Brønsted and Franklin acids.

[A Brønsted acid is a proton donor; conversely, a Brønsted base is a proton acceptor. A Franklin acid is a species which will give to a solvent a cation which is characteristic of the solvent system, e.g. $[\text{NO}]^+$ in the solvent N_2O_4 ; protons are not Franklin acids. A Lewis acid is any species which is an electron-pair acceptor. There are a wide range of species which can be described as Lewis acids, including BCl_3 , H^+ or transition metal ions. A Lewis base is an electron-pair donor. A superacid is an acidic medium with a Hammett acidity function $-H_0$ which has a value above 6. Superacids are upward of 10^6 times as strong as a 1M aqueous solution of strong acid (ref. G. A. Olah, G.K.S. Prakash and J. Sommer, Superacids, Wiley, Chichester, 1985.)

10

The solvent may in principle comprise any ionic liquid but the liquid normally comprises nitrate anions.

The cation will in practice comprise one or more organic cations, especially nitrogen heterocycles containing quaternary nitrogen and more especially *N*-substituted pyridinium or *N,N'*-disubstituted imidazolium. The substituents are preferably hydrocarbyl and more preferably alkyl, which may be branched, for example. The hydrocarbyl (e.g. alkyl) groups usually contain from 1 to 18 carbon atoms and some usually from 1 to 8 carbon atoms.

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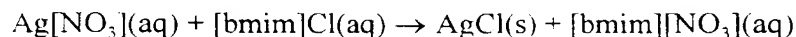
The cation may therefore be a disubstituted imidazolium ion where the substituent groups take the form $\text{C}_n\text{H}_{2n+1}$ for $1 \leq n \leq 8$, and the substituent groups are linear or branched groups. In preferred disubstituted imidazolium ions one substituent has $n=1, 2, 3$ or 4 (of which methyl is particularly preferred) and the other has $n=2, 3, 4, 5, 6, 7$ or 8 (of which octyl, hexyl and more particularly C_4 especially butyl are preferred, linear groups are preferred). Alternately, the cation might be a substituted tetra-alkylammonium ion, where the alkyl groups take the form of $\text{C}_n\text{H}_{2n+1}$ for $1 \leq n \leq 6$, and are linear or branched groups. A preferred example is tetrabutylammonium. However the alkyl groups might be of different lengths. Alternatively, the cation might be a substituted pyridinium ion, where the substituent group also takes the form $\text{C}_n\text{H}_{2n+1}$ for $1 \leq n \leq 8$, and the substituent groups are linear or branched groups; suitable substituents include butyl, 2-(2-methyl)propyl, 2-butyl and octyl but straight chain alkyl, especially butyl, is preferred.

30

Of course, minor quantities of contaminants may be present, e.g. protonated – methylimidazole in 1-butyl-3-methylimidazolium.

- 5 The nitrate-based ionic liquids of WO 98/06106 may be prepared by mixing aqueous silver(I) nitrate together with an appropriate organic halide. By way of example, one such ionic liquid is prepared by mixing together solutions of aqueous silver(I) nitrate and 1-butyl-3-methylimidazolium chloride ([bmim]Cl). Silver chloride is precipitated and the liquid 1-butyl-3-methylimidazolium nitrate is formed:

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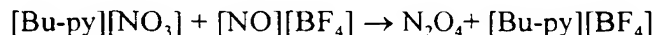


The product may be purified by filtration and removing excess water from the filtrate.

- 15 1-hexyl-3-methylimidazolium nitrate is prepared by a similar method and this material is also a liquid at room temperature.

Alternative cations to pyridinium and imidazolium include quaternary phosphonium cations, e.g. tetrahydrocarbylphosphonium. Suitable hydrocarbyl groups are as described
20 above in relation to pyridinium and imidazolium cations. Examples include unsymmetrically substituted phosphonium cations.

“The agent added to the ionic liquid to enable the oxidising process to occur more efficiently is typically an acid”, notably a Brønsted acid (e.g. HNO_3 or H_2SO_4) or a
25 Franklin acid. for example $[\text{NO}^+]$, serving in either case to make the medium more oxidisingly reactive towards substrates such as, for example, UO_2 or PuO_2 . In other words, one class of oxidising ionic liquids contains an oxidant comprising nitrate and a promoter thereof. The agent when combined with the ionic liquid may react with the ionic liquid to create a new species which is also an ionic liquid. Thus, $[\text{NO}][\text{BF}_4]$ is
30 believed to react with the nitrate salts of organic cations to form the tetrafluoroborate(III) salt of the cation. An exemplary reaction is:



wherein Bu-py is 1-butylpyridinium, and $[\text{Bu-py}][\text{BF}_4]$ is an ionic liquid.

5 Whilst the methods and ionic liquids described in WO 98/06106 are suitable for general use and, in particular, use in nuclear fuel reprocessing, we have now found an advantageous method which is an improvement over the prior art. In particular, WO 98/06106 does not describe clear separation and/or product recovery steps.

10 According to the present invention we provide a method for treating or reprocessing spent nuclear fuel to substantially separate fissile material from other components of irradiated fuel which comprises dissolving the spent fuel or constituent parts of the spent fuel in an ionic liquid. By the term substantially separate is meant partially separate, but preferably completely separate.

15

By the term other components of irradiated fuel, it is intended to include fission products, lanthanides, actinides and/or cladding materials. The method of the invention may preferentially also include the step of treating the ionic liquor, resulting from the step of dissolving spent nuclear fuel in an ionic liquid, by solvent extraction to separate the fissile
20 material from other components of irradiated fuel.

The ionic liquid is preferably an oxidising ionic liquid as described in WO 98/06106, which is incorporated herein by reference, particularly one containing an acid, e.g. a Brønsted, Lewis, Franklin or superacid; although Brønsted and Franklin acids are
25 preferred. Where an oxidising ionic liquid is used, the process involves oxidation of U(0) or U(IV) (normally as UO_2) to U(VI) and usually of Pu(IV) (normally as PuO_2) to Pu(VI); for example, uranium dioxide is oxidised to *trans*-dioxouranium(VI) in complexed form and plutonium dioxide to *trans*-dioxoplutonium(VI) in complexed form. Whatever the ionic liquid solvent, the dissolution of plutonium and uranium for recycling will normally
30 involve the unavoidable dissolution of other components of the irradiated fuel. The reprocessing methods form a fissile material optionally in the form of an intermediate or final nuclear fuel product, e.g. a gel, a powder, a master batch material, a fuel pellet, a fuel

pin or a fuel assembly. The dissolution may involve dissolution of the cladding of a fuel rod, e.g. a stainless steel or magnesium alloy cladding or a zirconium alloy cladding such as that sold under the trade mark Zircaloy; after irradiation of fuel, Zircaloy cladding has a passivating oxide coating and dissolution of Zircaloy cladding therefore involves non-oxidative dissolution of oxidised Zircaloy (zirconium alloy). The dissolution of the Zircaloy may be oxidative or non-oxidative. As an alternative to chemical removal of the cladding, as for example by dissolution in an ionic liquid, it may be removed prior to the dissolution of the fuel in the ionic liquid, whether by mechanical or chemical means.

Accordingly, one class of methods comprises contacting zirconium alloy clad irradiated fuel with an ionic liquid to dissolve the cladding and the fuel. For use in dissolving cladding the ionic liquid preferably contains sulfate and may contain sulfuric acid which has been found to react with the zirconium oxide layer on Zircaloy cladding. These methods may include immersing individual fuel pins or fuel assemblies in the ionic liquid within a suitable vessel.

A second class of methods includes the step of rupturing the cladding mechanically to expose the fuel pellets to the ionic liquid. In other methods, the fuel rod is placed initially in a first ionic liquid for dissolving the cladding and subsequently in a second ionic liquid for dissolving the uranium and plutonium or, optionally, compounds thereof. For dissolving fuel rods such as uranium or plutonium, a nitrate ionic liquid is preferred.

The dissolving of cladding may be carried out as a separate step to the dissolving of fuel, in which case different ionic liquids may be used. If the process of dissolving cladding and fuel is carried out as a single step then a mixed ionic liquid may optionally be used, eg a nitrate and sulfate ionic liquid mixture.

According to a yet further feature of the invention a solvent extraction step may be included to remove uranium and/or plutonium. In one aspect, the solution resulting from the dissolution of the fuel is treated to extract other components of irradiated fuel, after which the uranium and plutonium are separated from the ionic liquid. The uranium and plutonium may be removed together or they may be separated, in which latter case the

ionic liquid liquor is subjected to a uranium/plutonium split operation. The removal of uranium and plutonium may comprise selective dissolution step. Alternatively a fractional crystallisation may be used to bring about the removal of bulk uranium from the other components of irradiated fuel. The selective dissolution may be conducted before or
5 after extraction of other components of irradiated fuel, however it is preferable that a dissolution step is carried out before an extraction step.

The other components of irradiated fuel are suitably removed using a solvent extraction technique, for example one involving the contacting of the ionic liquid solution with a
10 hydrophilic phase, especially an aqueous medium or another ionic liquid into which the other components of irradiated fuel and any Zr are extracted. In another class of embodiments, the ionic liquid solution is contacted with a hydrophobic phase, especially an organic solvent, for example a straight chain hydrocarbon (normally a straight chain alkane) or a mixture of such hydrocarbons, into which the uranium and plutonium are
15 extracted. The solvent extraction technique may involve procedures, such as, for example, oxidation/reduction and/or complexing, to change the solubility properties of one or more selected species in order to control the partition of such species between the two phases.

20 Thus, some methods include the complexing of one or more dissolved species to change their relative solubilities in the two solvents. In one procedure, TBP (tributyl phosphate) is added to the second phase with which the ionic liquid solution is contacted, in order to complex dissolved uranium and plutonium and thereby effect transfer of those species to the second phase. As an example of the use of oxidation or reduction, it may be
25 mentioned that any uranium/plutonium separation may involve the selective reduction of one of the species into an oxidation state where the reduced or non-reduced species may be selectively extracted into another phase, for example an aqueous or organic phase or another ionic liquid. A reagent for the selective reduction of Pu rather than U is stabilised U(IV) ions. An example of this in Purex reprocessing is the use of U(IV) stabilised by
30 hydrazine.

The invention includes methods in which there is sequential dissolution of different components of the irradiated fuel. In particular, some processes involve a first ionic liquid dissolving the uranium, a second ionic liquid dissolving the plutonium and a third the fission products, not necessarily in this order.

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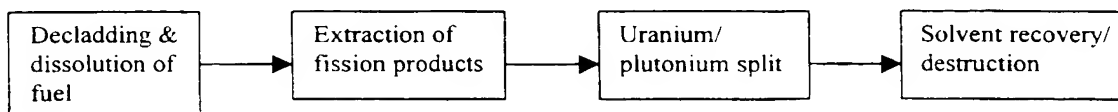
An additional method of bringing about the precipitation of dissolved metals, is via a reduction in temperature of the ionic liquid, in which the uranium is dissolved. A separation process for different metals would be via fractional crystallisation. This particular method further distinguishes the use of ionic liquids from conventional molten
10 salts, since it is impracticable to utilise the method with molten salts as such salts would solidify at lower temperatures.

The uranium, plutonium and fission products may be recovered from the two or three product streams. In those cases in which the product streams have an ionic liquid as
15 solvent, the precipitation of dissolved metals can be induced by changing the acidity and basicity of the ionic liquid by adding or subtracting further ionic components from it. Alternatively precipitation can be brought about by the addition of non-ionic components. For example the precipitation can be brought about by the addition of organic solvents which are miscible or slightly miscible with the ionic liquid. For example in the case of
20 the 1-butyl-3-methyl-imidazolium nitrate, ethyl acetate can be added to bring about the precipitation of a uranium compound. Ethyl acetate is slightly miscible with the ionic liquid, and at the point when the system just becomes biphasic through addition of ethyl acetate, precipitation is optimised.

25 Volatile non-ionic components added to the ionic liquid can be recovered from the ionic liquid by distillation. The ionic liquid is not volatile. This allows both the organic solvent and the ionic liquid to be recycled to the process.

30 An alternative means of precipitation is the addition to the ionic liquid of an oxidising or reducing agent.

A preferred process is illustrated by the following flowsheet:



- 5 In a second aspect, the ionic liquid liquor containing dissolved fuel and optionally dissolved cladding is subjected to electrochemical treatment to recover the dissolved uranium and plutonium. In one process, the liquor is subjected to electrolysis to deposit the uranium on the cathode as uranium oxide, a uranium compound or uranium metal; the dissolved plutonium may be recovered by a similar route. In some methods, dissolved
- 10 plutonium is co-deposited on the cathode with the uranium, irrespective of whether the metals are deposited in the metallic state (in the (0) oxidation state), as complexes or as oxides. Such co-deposition is useful in the manufacture of mixed oxide fuels.

Techniques for selecting the ion or ions to be deposited by electrodeposition are well

15 known in the molten salts and metallurgical industries and do not require detailed explanation here. However, it may be noted that all metal ions in a solution will have a different electrode reduction potential which is required to reduce the ion to a lower positive valency, or to reduce it to zero valency. Electrode reduction potentials are unique to the element, to the valency of the ion to the solvent and to the presence of other ions or

20 molecules. If a potential is applied across a solution then all metal ions with a more positive potential will be deposited on the cathode. Metal ions with a more negative potential will remain in solution. Once a particular ion has been removed from the solution, the electrode can be removed and replaced with a new one, run at a slightly more negative potential, for the deposition of the next metal with a more negative reduction

25 potential. If it is the desire to deposit two metals together, then a potential more negative than the reduction potential for both ions is applied to reduce them together.

The cathode material may be selected from known cathode materials, for example. Exemplary materials are carbon, especially glassy carbon, and tungsten.

30

The ionic liquid is optionally subjected to one or more intermediate steps between dissolution of the fuel and electrodeposition of dissolved species: for example, the ionic

liquid may be treated to reduce the uranium, either by the addition of a reducing agent or by an additional electroreduction step.

After the oxidative dissolution of the uranium oxide together with other soluble
5 components into the ionic liquid, there is a choice of process steps. Amongst these, two are outlined below, although this description is not intended to be limiting.

a) Fractional crystallisation of a uranium compound, and filtration and recovery of
this compound. This fractional crystallisation step may be a crude purification of
10 the uranium product. The remaining liquor containing fission products, actinides, lanthanides and plutonium can be subjected to further precipitation, or to electrochemical extraction to separate further uranium and/or plutonium.

b) An electrochemical step can be employed on the bulk of the solution to bring
15 about the separation of uranium and plutonium, from the other components of irradiated fuel.

Optionally, before conducting the electrochemical step the fuel, eg uranium or plutonium, may be purified, for example, by recrystallisation from an ionic liquid.

20

The electrochemical step may require that any excess acid is removed from the system or neutralised. If this is not the case, then any electrodeposited product may be re-oxidised and dissolved by the remaining acid present. Methods of removing the acid include one or more of the following:

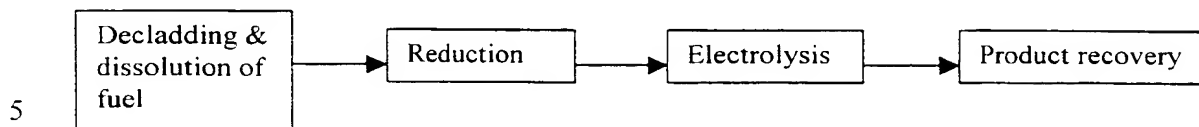
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(i) ensure that there is an excess of fuel present, to ensure that all acid reacts (excess acid is probably required to drive the process);

(ii) reduce remaining acid (i.e. the proton) electrochemically to hydrogen;
30 and/or

(iii) boil off excess acid, the ionic liquid remaining behind.

A preferred embodiment is illustrated by the following flowsheet:



The process illustrated in the flowsheet includes addition of a reductant to the liquor resulting from dissolution and passage of the resultant liquor to an electrochemical apparatus, e.g. an electrochemical bath, where the uranium species is reduced by the application of a current across the electrodes and is deposited at a cathode as uranium metal or another uranium compound. The deposited uranium will be removed from the electrode and passed to a further step for removal of entrapped ionic liquid. A similar process is used to recover dissolved plutonium.

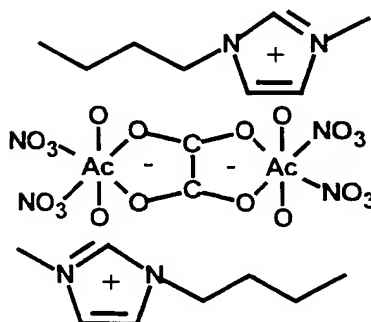
The fuel material produced by the method of the invention is novel per se, in that it has a unique dimeric structure, in which two atoms of fuel material form a dimeric species comprising a dicarboxylate bridge. Although, various dicarboxylates may be used, for example, oxalate, malonate, succinate, glutarate, adipate or pimelate; a preferred bridge moiety is oxalate.

Thus according to a further feature of the invention we provide a fuel material comprising a dimeric species containing two fuel atoms bridged by a dicarboxylate moiety.

In particular we provide a fuel material in which the fuel is uranium. The preferred fuel is uranium. The preferred fuel material has a structure:

25

30



in which Ac is Pu or U, preferably U.

Although the structure given in I above is representative, it is understood that bonding of the nitrate groups is via one of the oxygen atoms.

5

The fuel material of the invention also provides a unique X-ray diffraction pattern. Thus according to the invention we provide a fuel material a molecular structure as shown in Fig. 2 which is derived by X-ray diffraction.

10 The method of the invention will now be illustrated but in no way limited with reference to the following Examples and the accompanying drawings

Example 1

15

Preparation of 1-butyl-3-methylimidazolium nitrate ionic liquid

1-Methylimidazole was distilled under vacuum and stored under dinitrogen prior to use. 1-Butyl-3-methylimidazolium or 1-alkylpyridinium salts were prepared by direct reaction
20 of the appropriate alkyl halide with 1-methylimidazole or pyridine, respectively, and recrystallised from ethanenitrile and ethyl ethanoate.

Nitrate ionic liquids were all prepared by methods analogous to the following method used to prepare 1-butyl-3-methylimidazolium nitrate.

25

1-butyl-3-methylimidazolium chloride (8.04 g, 46.0 m mol) was dissolved in water (15 cm³). To this solution a solution of silver(I) nitrate (7.82 g, 46.0 m mol) in water (20 cm³) was added. A white precipitate (silver(I) chloride) formed immediately. The mixture was stirred (20 min) to ensure complete reaction, and was then filtered twice
30 through a P3 sintered glass funnel to remove the white precipitate (the second filtration was generally necessary to remove the final traces of precipitate). The water was removed on a rotary evaporator, yielding a yellow or brown viscous liquid, sometimes

containing small black solid particles. This crude product, 1-butyl-3-methylimidazolium nitrate, was dissolved in a small quantity of dry acetonitrile, and decolourising charcoal was added to the solution. This was then stirred (30 min) and filtered through Celite®. The acetonitrile was removed under vacuum, and the pale yellow ionic liquid product
5 then dried by heating *in vacuo* (ca. 50 °C, 2-3 d). Some discoloration of the product occurred if the heating was too vigorous. Residual silver(I) chloride was removed by electrolysis; silver metal is electroplated at the cathode; and chlorine gas is evolved at the anode. The resulting ionic liquid was stored under dinitrogen to exclude moisture.

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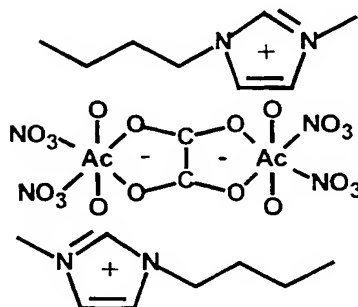
Example 2

Results of crystallisation process

15 The following procedure and results, back up the crystallisation process. In a round bottomed flask, 9.32 g [bmim][NO₃], 4.73 g of conc. aqueous HNO₃, and 4.00 g UO₂ were combined. This mixture was stirred and heated to 70°C for 16 hours. The bright yellow solution which formed, was allowed to cool to room temperature, and to stand overnight. This resulted in the formation of pale yellow crystals. These were removed from the
20 solution by vacuum filtration, using a P4 frit. The vacuum was maintained for up to eight hours, in order to bring about as much removal of the ionic liquid as possible. The crystals formed were then rinsed with cold ethyl acetate to remove any residual ionic liquid. A uranyl salt has been identified analysis of which has identified the molecular as C₁₈H₃₀N₈O₂₀U₂, and the elemental weight percents are: 18.73% C; 2.62% H; 9.71% N;
25 27.72 % O; and 41.23 % U.

X-ray diffraction studies have determined the structure as that shown below:

30



5 and generally of the structure shown in Figure 2, in which the Cell Parameters are:

$$A = 15.452$$

$$B = 20.354$$

$$C = 10.822$$

10 $\beta = 106.84$

Example 3

15

Electrochemical Reduction of the Uranyl Salt

0.2655 g (0.23 m mol) of the uranyl salt, precipitated from a uranyl solution in [bmim][NO₃] + HNO₃ by cooling (as explained in Example 2) and recrystallised from acetonitrile, was added to 28.12 g pure [bmim][NO₃] (ca. 25 mL) and dissolved by
20 heating (ca 50°C) and stirring while sparging with dry nitrogen. Complete dissolution occurred within 15 minutes. Nitrogen sparging was continued for one hour.

Electrochemical reduction of the uranyl salt may produce UO₂ which is insoluble in the
25 ionic liquid and should precipitate from solution. Every mole of uranyl salt is believed to produce two moles of UO₂. Therefore, complete reduction of 0.23 m mol of the uranyl salt to UO₂ should yield 0.46 m mol UO₂. Furthermore, since each mole of UO₂ produced

requires two mole equivalents of electrons, the total charge required during the production of 0.46 m mol UO_2 should be 88.8 C.

An electrolysis cell was set up in a three-electrode cell with the uranyl solution as the bulk solution. The reference electrode was a silver wire immersed in a 0.1 mol L^{-1} solution of AgNO_3 in $[\text{bmim}][\text{NO}_3]$ separated from the bulk solution in a glass tube with a porous vycor tip. The counter electrode was a platinum coil immersed in pure $[\text{bmim}][\text{NO}_3]$ separated from the bulk solution in a glass tube with a glass frit. The working electrode was a flag (ca 3 cm x 2 cm x 0.1 cm) formed from a sheet of glassy carbon.

Electrolysis was carried out on the stirred uranyl solution under a dry nitrogen atmosphere by holding the cathode potential at -1.5 V versus Ag(I)/Ag . During electrochemical reduction of the uranyl salt, the cathode became passivated and electrolysis was halted, perhaps by the adsorption of the UO_2 product. Two techniques were used simultaneously to keep the cathode from becoming passivated. Dry nitrogen was bubbled across the electrode remove passivating material such as adsorbed UO_2 . Instead of holding the cathode at -1.5 V constantly, the working electrode potential was periodically stepped to +1.0 V (where it acts as an anode). Typically, the working electrode was held at 1.5 V for 9.6 s and pulsed to +1.0 V for 0.4 s. Used in conjunction, nitrogen sparging and potential pulsing kept the electrode from passivating.

During the electrolysis, the solution lost the bright yellow colour associated with uranyl salts and turned brown. Toward the end of the electrolysis, a dark brown precipitate was noted. After the passage of 95 C, electrolysis was halted as the current dropped dramatically. Voltammograms recorded at a glassy carbon disk working electrode before and after electrolysis (Figure 1) demonstrate the elimination of uranyl from the solution. Scans of the electrode potential were initiated at 0 V, scanned to the cathodic limit of the ionic liquid, reversed and scanned to anodic limit, and then returned to 0 V.

Series 1 (blue) shows a voltammogram recorded in the neat solution. The electrochemical window of the ionic liquids is demonstrated as stretching from ca. -2.2V, where the organic cation is reduced, to ca. +1.5V, where nitrate is oxidised.

Series 2 (violet) shows a voltammogram recorded in the 0.1 mol L⁻¹ uranyl solution prior to electrolysis. The wave with a peak around -0.9 V represents the reduction of uranyl. A much smaller anodic wave can be seen around 0 V. Lack of an anodic wave of equal
5 size during the reverse scan indicates that the reduction is chemically irreversible. The broadness of the cathodic wave indicates slow electron transfer.

Series 3 (yellow) shows a voltammogram recorded in the bulk solution after electrolysis. There is very little current above the background current of the ionic liquid (blue). A
10 slight rise in current around -0.2 V indicates that the electrolysis was not 100% complete.

The solution was diluted with acetone (to make the solution less viscous) and the precipitate was collected by vacuum filtration through size P4 glass frit.

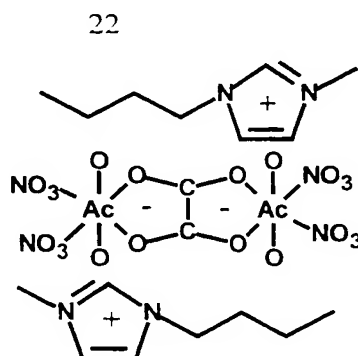
CLAIMS

1. A method for treating or reprocessing spent nuclear fuel to substantially separate
5 fissile material from other components of irradiated fuel which comprises dissolving the spent fuel or constituent parts of the spent fuel in an ionic liquid.
2. A method according to Claim 1 which includes a separate step of solvent
extraction to remove uranium.
- 10 3. A method according to Claim 1 which includes a separate step of solvent extraction to remove plutonium.
4. A method according to Claim 1 which includes a separate step of solvent
15 extraction to remove uranium and plutonium together.
5. A method of Claim 1 in which the liquor is contacted with a hydrophilic solvent into which the fission products are extracted.
- 20 6. A method of Claim 5 in which the hydrophilic solvent comprises an aqueous medium or an ionic liquid.
7. A method of Claim 1 in which the liquor is contacted with a hydrophobic solvent into which the fission products are extracted.
- 25 8. A method of Claims 2 to 4 in which the liquor is contacted with a hydrophobic solvent into which the fissile material is extracted.
9. A method of Claim 8 wherein the fissile material is precipitated by adjusting the
30 pH of the solvent into which the fissile material is extracted.

10. A method of Claim 8 wherein the fissile material is precipitated by adding a non-ionic component to the solvent into which the fissile material is extracted.
11. A method of Claim 8 wherein the fissile material is precipitated by fractional
5 crystallisation.
12. A method of Claim 8 in which the hydrophobic solvent comprises one or more straight chain hydrocarbons.
- 10 13. A method of Claim 1 in which the solvent extraction involves controlling the solubility properties of one or more species by complexing, oxidising or reducing the species.
14. A method of Claim 1 wherein the nuclear fuel comprises a cladding and the
15 method includes dissolution of the cladding in the ionic liquid.
15. A method of Claim 14 in which the cladding is zirconium alloy cladding.
16. A method of any of Claims 1 to 13 wherein the nuclear fuel comprises a cladding
20 and the method comprises removal or rupturing of the cladding before dissolution of the fuel.
17. A method of Claim 1 in which the ionic liquid contains an agent to enhance the oxidising ability of the ionic liquid, to enable it to oxidise U(IV) to U(VI) and possibly
25 Pu(IV) to Pu(VI).
18. A method of Claim 17 in which the ionic liquid contains both nitrate anions and a Brønsted or superacid.
- 30 19. A method of Claim 18 in which the acid is a Brønsted acid or Franklin acid.

20. A method of Claim 19 in which the acid is HNO_3 , H_2SO_4 or $[\text{NO}]^+$, e.g. from $[\text{NO}][\text{BF}_4]$.
21. A method according to Claim 20 in which the $[\text{NO}]^+$ is from $[\text{NO}][\text{BF}_4]$.
- 5 22. A method of Claim 1 in which the ionic liquid is based on a 1,3-dialkyl imidazolium nitrate and wherein the alkyl groups may be the same or different.
23. A method of Claim 1 in which the ionic liquid is based on a sulfate.
- 10 24. A method according to Claim 23 wherein the ionic liquid is based on $[\text{bmim}]_2[\text{SO}_4]$.
25. A method according to claim 23 wherein the ionic liquid is based on
- 15 $[\text{bmim}][\text{HSO}_4]$.
26. A method of Claim 1 which is a method for reprocessing nuclear fuel to form a fissile material optionally in the form of a gel, a powder, a master batch material, a fuel pellet, a fuel pin or a fuel assembly.
- 20 27. A method for treating or reprocessing spent nuclear fuel to separate or partially separate fissile material from fission products, in which method the fuel is dissolved in an ionic liquid and the resultant liquor is subjected to electrolysis to deposit dissolved uranium compound at the cathode.
- 25 28. A method of Claim 27 wherein the nuclear fuel comprises zirconium alloy cladding and the method includes dissolution of the cladding in the ionic liquid.
29. A method of Claim 27 wherein the nuclear fuel comprises a cladding and the
- 30 method comprises removal or rupturing of the cladding before dissolution of the fuel.

30. A method of any of Claims 27 to 29 in which the ionic liquid is subjected to one or more intermediate steps between dissolution of the fuel and electrodeposition of dissolved uranium.
- 5 31. A method of Claim 30 in which the intermediate steps comprise treatment of the ionic liquid to reduce dissolved uranium.
32. A method of any of Claims 27 to 31 which further comprises subjecting the liquor, before or after electrodeposition of dissolved uranium, to electrolysis to deposit dissolved
10 plutonium or a plutonium compound at the cathode.
33. A method of any of Claims 27 to 31 in which dissolved plutonium is co-deposited on the cathode with the uranium.
- 15 34. A method of any of Claims 27 to 31 which is a method for reprocessing nuclear fuel to form a fissile material optionally in the form of a gel, a powder, a master batch material, a fuel pellet, a fuel pin or a fuel assembly.
35. A fuel material comprising a dimeric species containing two fuel atoms bridged by
20 a dicarboxylate moiety.
36. A fuel material according to Claim 35 wherein the fuel atoms are either both U or both Pu.
- 25 37. A fuel material according to Claim 36 wherein the fuel atoms are both U.
38. A fuel material according to Claim 35 wherein the dicarboxylate moiety is oxalate.
39. A fuel material according to Claim 36 having a structure
30



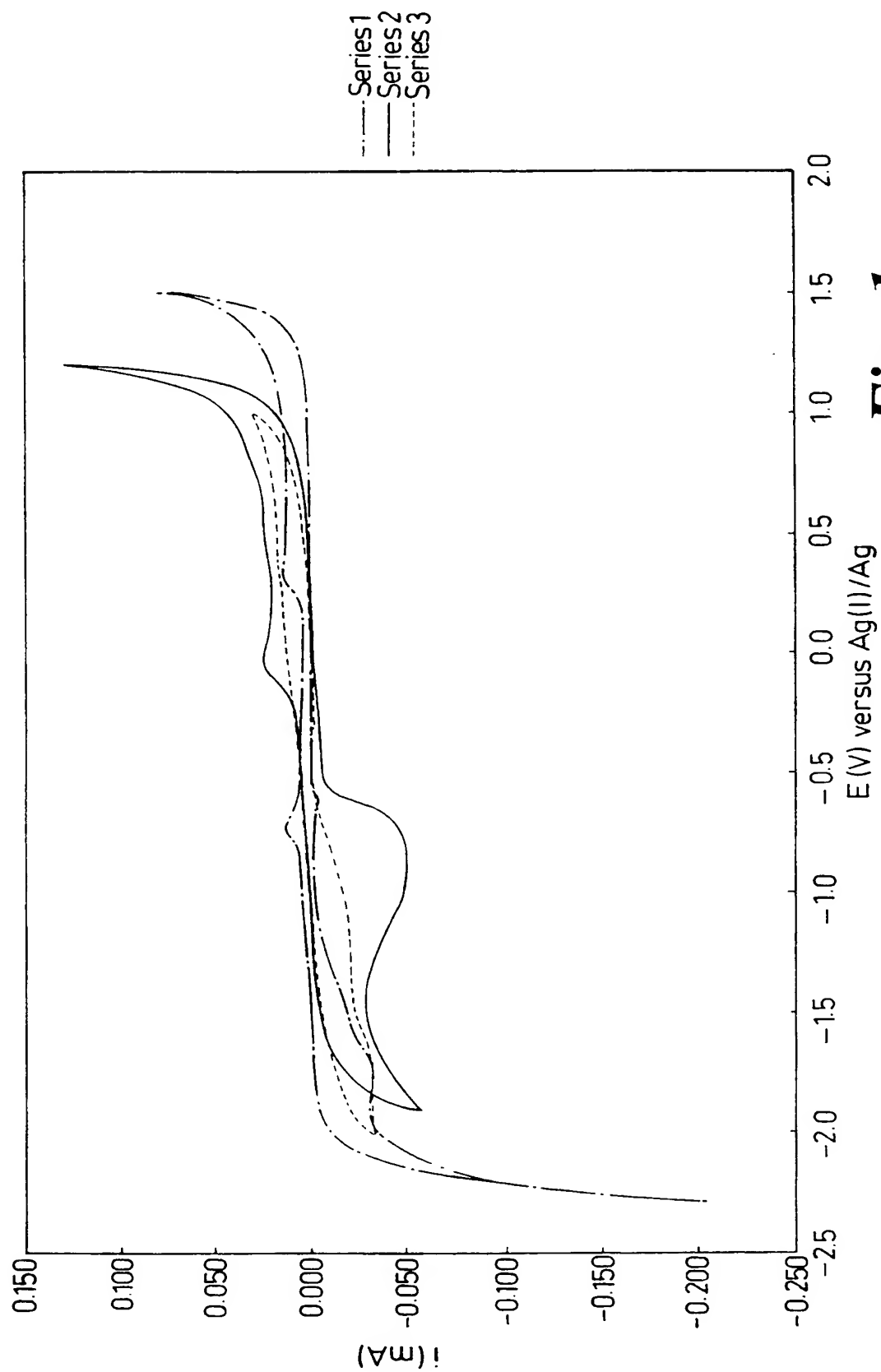
wherein Ac is Pu or U.

5 40. A fuel material according to Claim 39 wherein Ac is U.

41. A fuel material according to Claim 35 which has a molecular structure substantially as defined by Figure 2.

10 42. A method for treating or reprocessing spent nuclear fuel substantially as herein before described with reference to the accompanying description and drawing.

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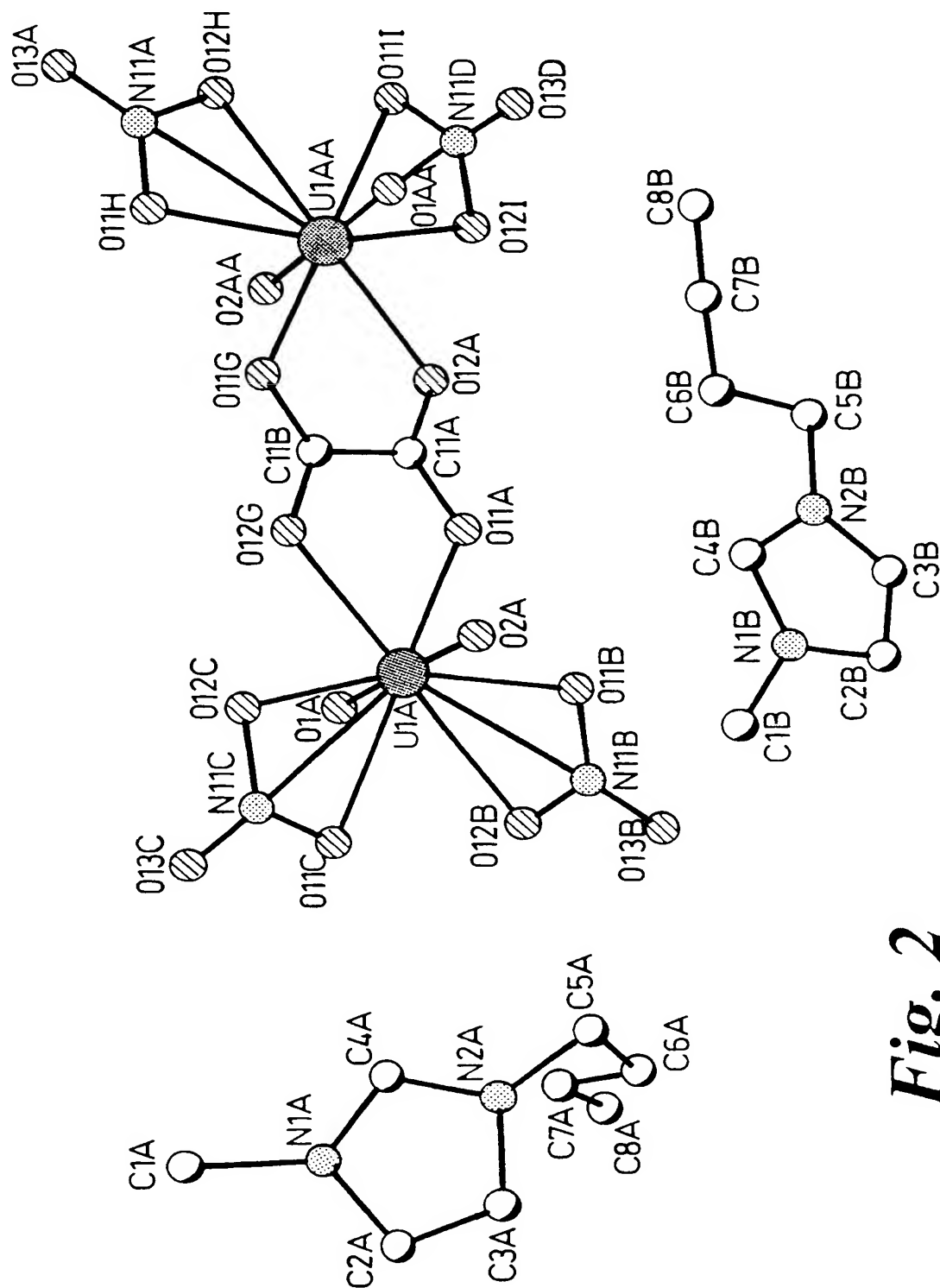


Fig. 2

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/00246

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 G21C19/48 G21C3/58 C07F5/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G21C C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 98 06106 A (BRITISH NUCLEAR FUELS PLC :GORDON CHARLES MCINTOSH (GB); FIELDS MA) 12 February 1998 see the whole document ---	1, 14-16, 18-22, 26-29, 34, 42
X	LEGROS, JEAN P. ET AL: "Structure of the.mu.-oxalatobis' dioxalatodioxouranium (VI)! ion '(UO2)2(C2O4)5!6-" ACTA CRYSTALLOGR., SECT. B (1976), B32(8), 2497-503 CODEN: ACBCAR, 1976, XP002106906 see page 2500 --- -/--	35-38



Further documents are listed in the continuation of box C.



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Date of the actual completion of the international search

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Date of mailing of the international search report

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Name and mailing address of the ISA

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NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

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Brothier, J-A

INTERNATIONAL SEARCH REPORT

Int. Application No

PCT/GB 99/00246

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication where appropriate, of the relevant passages	Relevant to claim No
X	<p>SHCHELOKOV, R. N. ET AL: "Coordination compounds of uranyl of the μ_2-oxalato series"</p> <p>KOORD. KHIM. (1982), 8(4), 518-22 CODEN: KOKHDC, 1982, XP002106907</p> <p>see page 176, line 34</p> <p style="text-align: center;">---</p>	35-38
X	<p>BESSONOV, A. A. ET AL: "Electronic absorption spectra of some plutonium (VI) oxalates"</p> <p>RADIOKHIMIYA (1996), 38(3), 223-225 CODEN: RADKAU; ISSN: 0033-8311, 1996, XP002106908</p> <p>see page 224</p> <p style="text-align: center;">---</p>	35, 36, 38
X	<p>MOSKVIN, A. I.: "Thermodynamic characteristics of the formation of actinide compounds in solid form. I. Energy and entropy of a crystalline lattice. Heats of formation and heats of dissolution"</p> <p>RADIOKHIMIYA (1973), 15(3), 353-62 CODEN: RADKAU, 1973, XP002106909</p> <p>see page 357</p> <p style="text-align: center;">---</p>	35, 36, 38
A	<p>WO 96 32729 A (BRITISH NUCLEAR FUELS PLC ; FIELDS MARK (GB); WILSON PETER DAVID (G) 17 October 1996</p> <p>see the whole document</p> <p style="text-align: center;">---</p>	27, 32, 33
A	<p>WO 96 18459 A (BP CHEM INT LTD ; ELLIS BRIAN (GB)) 20 June 1996</p> <p>see the whole document</p> <p style="text-align: center;">-----</p>	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

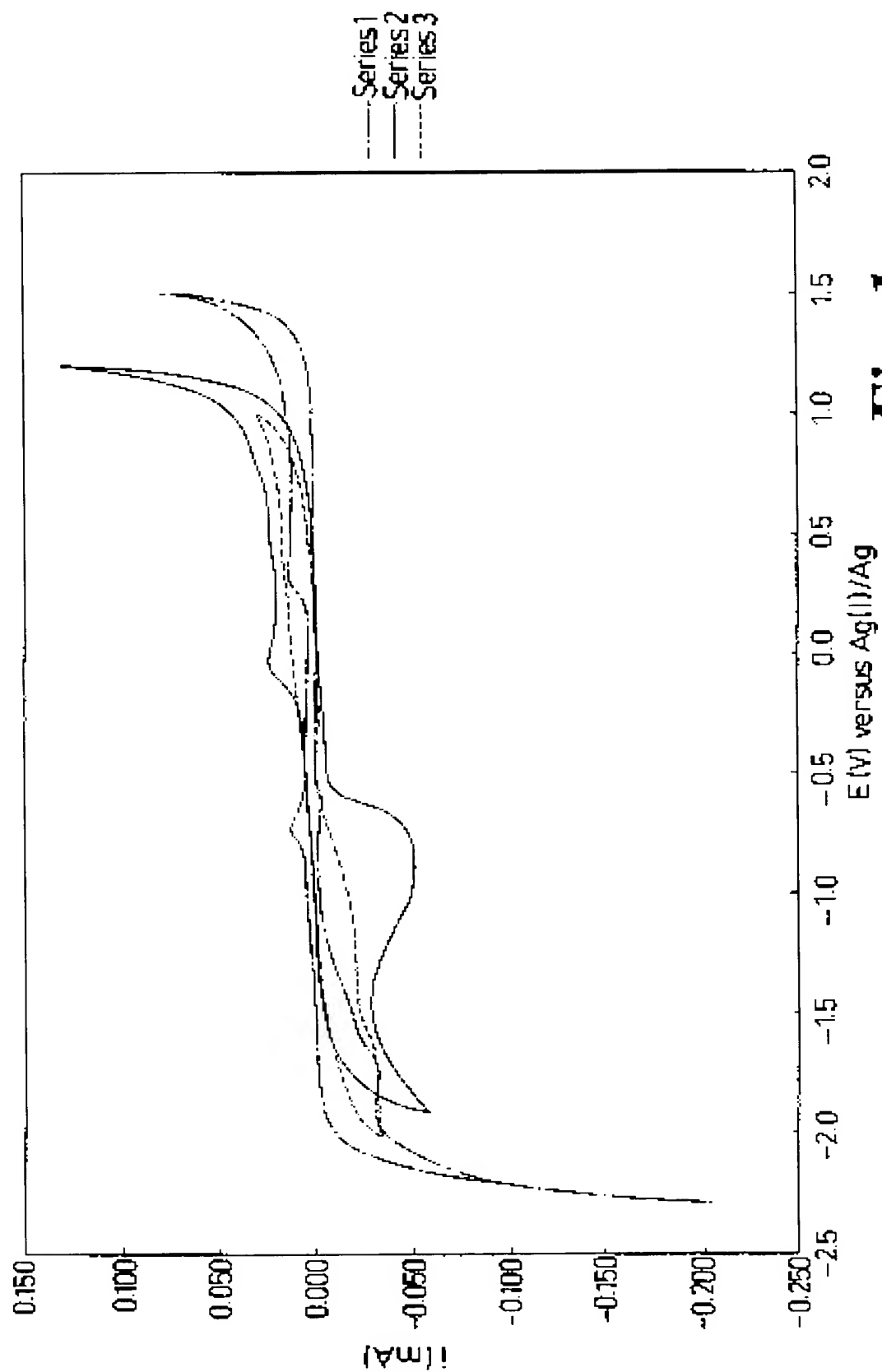
International Application No

PCT/GB 99/00246

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9806106 A	12-02-1998	AU 3703497 A	25-02-1998
WO 9632729 A	17-10-1996	NONE	
WO 9618459 A	20-06-1996	AU 3986495 A	03-07-1996
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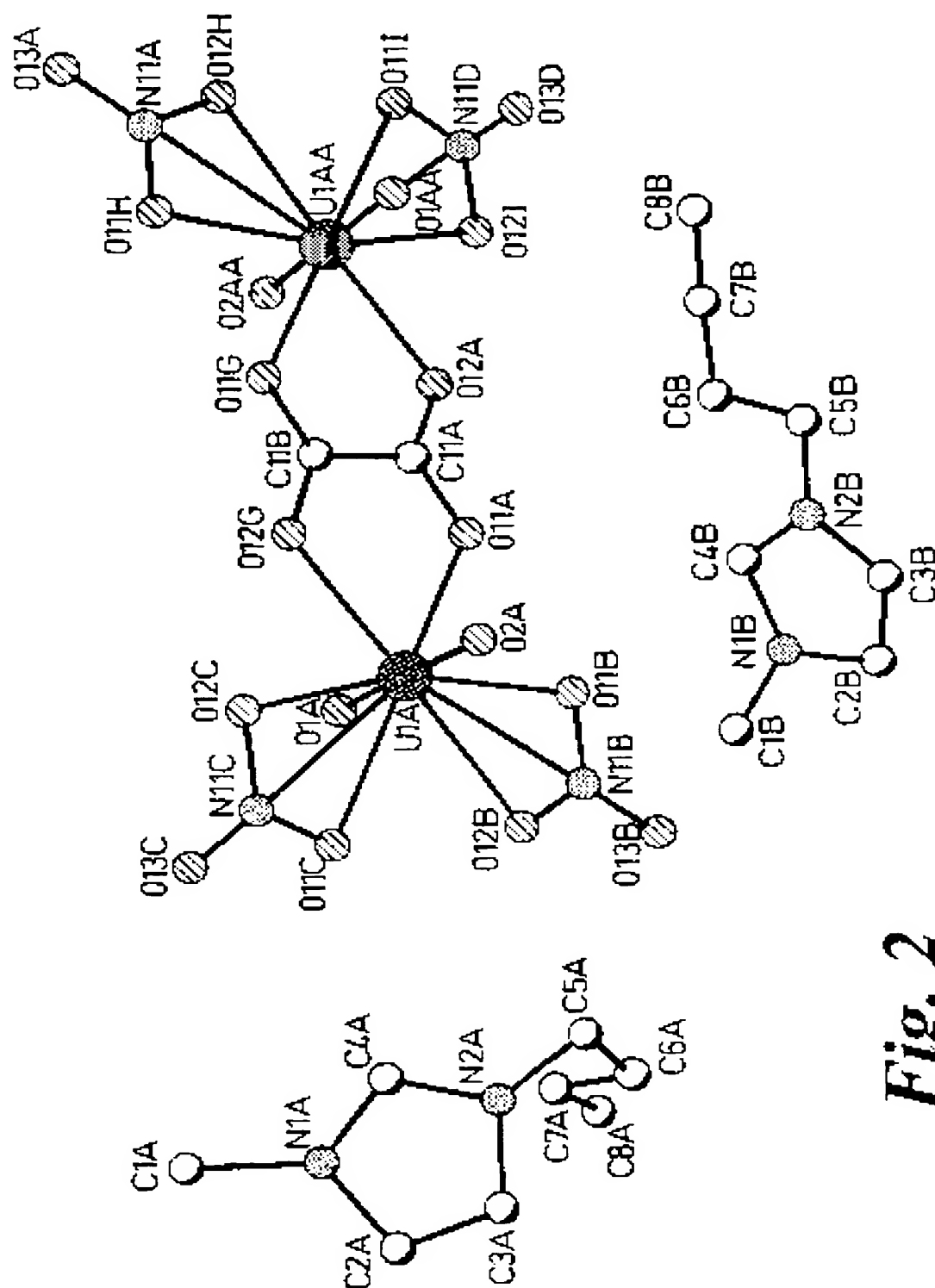


Fig. 2

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C01D 3/18, G21C 19/48	A1	(11) International Publication Number: WO 99/14160 (43) International Publication Date: 25 March 1999 (25.03.99)
(21) International Application Number: PCT/GB98/02743 (22) International Filing Date: 16 September 1998 (16.09.98) (30) Priority Data: 9719551.5 16 September 1997 (16.09.97) GB (71) Applicant (for all designated States except US): BRITISH NUCLEAR FUELS PLC [GB/GB]; Risley, Warrington, Cheshire WA3 6AS (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): FIELDS, Mark [GB/GB]; 22 Abbey Heights, Ireleth, Askam-in-Furness, Cumbria CA16 7HT (GB). THIED, Robert, Charles [GB/GB]; BNFL, Sellafield, Seascale, Cumbria CA20 1PG (GB). SEDDON, Kenneth, Richard [GB/GB]; School of Chemistry, The Queen's University of Belfast, Belfast BT9 5AG (GB). PITNER, William, Robert [US/GB]; School of Chemistry, The Queen's University of Belfast, Belfast BT9 5AG (GB). ROONEY, David, William [IE/GB]; School of Chemistry, The Queen's University of Belfast, Belfast BT9 5AG (GB). (74) Agent: HARRISON GODDARD FOOTE; Belmont House, 20 Wood Lane, Leeds LS6 2AE (GB).		(81) Designated States: CA, CN, JP, KP, RU, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: TREATMENT OF MOLTEN SALT REPROCESSING WASTES (57) Abstract A method of removing from a metal salt ionic species contained therein involves contacting the metal salt with an ionic liquid to dissolve the metal salt, the ionic species or both. At least in the case where both the metal salt and the ionic species are dissolved, the resultant ionic liquid composition is treated to separate the ionic species therefrom and subsequently processed to recover the metal salt.		

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TREATMENT OF MOLTEN SALT REPROCESSING WASTES

This invention relates to the treatment of salts and, more particularly, the treatment of salts previously used in molten form in the reprocessing and treatment of nuclear materials.

Molten salts are known for their use as solvents and they have in fact been proposed for use in the reprocessing or treatment of irradiated fuels from light water reactors (LWRs) and fast reactors. In such a method, an irradiated fuel is dissolved into molten alkali metal chlorides. The dissolved uranium and plutonium species are extracted from the salt and, optionally, processed into fuel, and the molten salt is re-used. Eventually the molten salt becomes significantly contaminated with fission products which must be removed before the salt can be re-used. One process which uses molten salts for reprocessing irradiated fuel uses lithium chloride/potassium chloride eutectic [$\{\text{LiCl} + \text{KCl}\}$ eutectic] and another uses sodium chloride/potassium chloride eutectic [$\{\text{NaCl} + \text{KCl}\}$ eutectic]. When used herein, the term "molten salt" refers to a salt, or a mixture of salts, having inorganic cationic and anionic species, and having a melting point in excess of 100°C, usually at least 300°C. The term "metal salt", when used herein, refers to a material which gives rise to a molten salt when melted. In addition to chloride salts such as those mentioned above, other molten salts with which this invention may be concerned include fluorides and carbonates.

Recently, salts, mixtures of salts, or mixtures of components which produce salts, which melt below or just above room temperature have become known. (In the terms of this invention, a salt consists entirely of cationic and anionic species). Such liquids are known as "ionic liquids" although this term can be used for salts which melt at relatively high temperatures, including for example temperatures of up to 100°C. They normally include at least an organic cation. Common features of ionic liquids include a zero vapour pressure at room temperature, a high solvation capacity and a large liquid range (for instance, of the order of 300°C).

When used herein, the term "ionic liquid" refers to a salt, a mixture of salts, or a mixture of components which produce salts and which melts at a temperature up to 100°C and/or includes an organic cation.

5 Other ionic liquids are, for example, nitrates, fluoroborates, ethanoates or hexafluorophosphates, of which nitrates and fluoroborates are discussed in PCT/GB97/02057,. Mixtures of any of the previously described ionic liquids may likewise be used.

10 Known ionic liquids include halides such as an imidazolium halide, a pyridinium halide or a phosphonium halide as well as such materials in combination with, for instance, a metal halide such as aluminium chloride. Examples of ionic liquids include 1-ethyl-3-methylimidazolium chloride, *N*-butylpyridinium chloride, tetrabutylphosphonium chloride and a mixture of 1-ethyl-3-methylimidazolium chloride and aluminium(III)
15 chloride.

E. S. Lane, *J. Chem. Soc.* (1953), 1172-1175 describes the preparation of certain alkylpyridinium nitrate ionic liquids, including sec-butylpyridinium nitrate. No use of the liquids is mentioned but reference is made to the pharmacological activity of
20 decamethylenebis(pyridinium nitrate).

Ionic liquids based on various anions, including nitrate, fluoroborate and ethanoate, are disclosed by J S Wilkes et al., *J. Chem. Soc. Chem. Commun.*, 965-967 (1992). The use as solvents for catalysis of ionic liquids based on non-nucleophilic ions such as
25 tetrafluoroborate and hexafluorophosphate is described by Y. Chauvin et al., *Angew. Chem. Int. Edit. Engl.*, 34, 2698-2700 (1995).

L. Heerman et al., *J. Electroanal. Chem.*, 193, 289 (1985) describe the dissolution of UO_3 in a system comprising *N*-butylpyridinium chloride and aluminium(III) chloride.

30

WO 95/21871, WO 95/21872 and WO 95/21806 relate to ionic liquids and their use to catalyse hydrocarbon conversion reactions (e.g. polymerisation or oligomerisation of

olefins) and alkylation reactions. The ionic liquids are preferably 1-(C₁-C₄ alkyl)-3-(C₆-C₃₀ alkyl) imidazolium chlorides and especially 1-methyl-3-C₁₀ alkyl-imidazolium chloride, or 1-hydrocarbyl pyridinium halides, where the hydrocarbyl group is for example ethyl, butyl or other alkyl.

5

The present invention provides a method of removing from a metal salt ionic species therein, which method comprises contacting the metal salt with an ionic liquid to dissolve the metal salt, the ionic species or both, thereby to form a resultant ionic liquid composition and, at least in the case where both the molten salt and the ionic species are
10 dissolved, said ionic liquid composition is treated to separate the ionic species therefrom and subsequently processed to recover the metal salt.

The method of the invention has the advantage that it can be performed at relatively low temperatures (e.g. of about 50 °C or less), for example at temperatures at or close to room
15 temperature.

The ionic species with which this invention is concerned include ions of fission products, minor actinides, activation products, corrosion products, fuel additives and process
20 additives.

20

The metal salt is preferably an alkali metal halide or a mixture of alkali metal halides, for example a mixture of lithium chloride and potassium chloride or a mixture of sodium chloride and potassium chloride. Such alkali metal halide mixtures are suitably eutectics.

25 The species removed from the metal salt may comprise fission product ions, for example as their chlorides, fluorides or nitrates. Exemplary fission products include Cs, Sr, Ba and those of the actinides and lanthanides. The invention is particularly concerned with methods in which the ionic species comprise cations of the lanthanides (for example Sm, Gd and Ce) and the metals Cs, Sr and Ba.

30

In preferred processes, the metal salt and the ionic species are dissolved in the ionic liquid and known techniques may be used to separate the dissolved products. Suitable

separation techniques include salting out, electrochemical methods, precipitation and ion exchange. In one class of methods, the solution is treated to separate the ionic species, typically fission product chlorides, therefrom and subsequently processed to recover the metal salt.

5

Alternatively, a component from the metal salt and contaminant fission product mixture is dissolved in the ionic liquid. The presence of an insoluble component leads to the first step in the separation sequence.

10 In one preferred class of processes, $\text{LiCl} + \text{KCl}$ or $\text{NaCl} + \text{KCl}$, in either case containing dissolved fission products, is contacted at, for example, room temperature with an ionic liquid system in which the alkali metal halides as well as fission products to be separated therefrom are soluble. The invention contemplates in particular ionic liquids containing an organic halide, optionally in combination with a metal halide such as aluminium(III)
15 chloride; such ionic liquids include in combination with an imidazolium halide, a pyridinium halide or a phosphonium halide as well as these materials in combination with aluminium (III) chloride. Examples of organic halide ionic liquids include 1-ethyl-3-methylimidazolium chloride, *N*-butylpyridinium chloride and tetrabutylphosphonium chloride. Preferred ionic liquids include 1-ethyl-3-methylimidazolium chloride and a
20 mixture of basic (that is, Franklin basic) 1-ethyl-3-methyl-imidazolium chloride and aluminium(III) chloride (" $[\text{emim}]\text{Cl}-\text{AlCl}_3$ "). Of course, the foregoing ionic liquids may be used to dissolve salt compositions other than $\text{LiCl} + \text{KCl}$ or $\text{NaCl} + \text{KCl}$.

A further preferred option is combining the ionic liquids to form a mixture, such as 1-
25 ethyl-3-methyl-imidazolium chloride and 1-octyl-3-methyl-imidazolium chloride.

The composition of the $[\text{emim}]\text{Cl}-\text{AlCl}_3$ mixture determines whether the liquid has Franklin acidic, basic or neutral properties. A basic melt has an $\text{AlCl}_3:[\text{emim}]\text{Cl}$ ratio < 1.0 , whilst an acidic melt has an $\text{AlCl}_3:[\text{emim}]\text{Cl}$ ratio > 1.0 . A neutral melt has an
30 $\text{AlCl}_3:[\text{emim}]\text{Cl}$ ratio $= 1.0$.

The invention will now be described in more detail primarily in relation to alkali metal halide salts previously used in reprocessing and contaminated with fission products. It will be understood, however, that the invention may equally be applied to other metal salts, especially to remove contaminants.

5

Thus, in the treatment of salt compositions resulting from reprocessing and treatment of nuclear materials, the ionic liquid (e.g. basic [emim]Cl-AlCl₃) may be used to dissolve one or more of the alkali metal halide[s] and/or (usually by complexing) the bulk of the fission product halides (normally chlorides). If the alkali metal halide component of the composition is relatively insoluble in the ionic liquid, as in the case of NaCl in basic [emim]Cl-AlCl₃, the fission products may be leached into solution. Such leaching is desirably aided by reducing the particle size by, for instance, mechanically dividing (e.g. crushing or grinding) the salt.

The ionic liquid mixture is then treated to separate the alkali metal halides from the fission products, for example by using one or more techniques known per se for separating solutes. Suitable separation procedures include salting out, other precipitation methods, ion exchange, and electrochemical separation. The fission products may not have been completely dissolved in the ionic solvent because, for instance, they may be "locked" within the particles of an insoluble component. A further washing step may be necessary in these circumstances. In such cases, the invention normally includes the decontaminating of such insoluble residues remaining after the dissolution of the alkali metal halide composition. Each of the foregoing procedures will now be considered in turn with specific reference to the treatment of reprocessing salt compositions.

25 Salting Out of Chlorides

A majority of radioactive fission product halides (but not Cs halides) have lattice energies, which are considerably greater than those of the alkali metal halides. Thus, when the salts have been dissolved in an ionic liquid the fission product chlorides may be precipitated by the addition of a species (for example toluene, benzene or other organic solvent) which makes the ionic liquid more like an organic solvent, thereby destabilising the fission product complexes: as the ionicity of the solution decreases a fission product

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chloride is precipitated when the stabilisation energy of the complex in the solution becomes less than the lattice energy of the chloride. Thus, lanthanide and alkaline earth chlorides are generally precipitated before alkali metal chlorides.

- 5 The precipitated chlorides may in practice be pyrohydrolysed prior to disposal.

Alternatively the salt may be dissolved in water or similar solvent, the resulting solution being added to an ionic liquid. Upon removal of the water by evaporation, the soluble component(s) of the solute may be extracted into the ionic liquid and any components
10 which are insoluble in the ionic liquid will form a precipitate.

Precipitation of Phosphates

As an alternative to precipitation by salting out (or even to supplement it), fission product
15 salts, especially phosphates, may be precipitated from the ionic liquid solution by addition of, in particular, a phosphate such as, for example, Na_3PO_4 or $\text{K}[\text{H}_2\text{PO}_4]$.

Ion Exchange

20 After precipitation of lanthanide fission products as phosphates, the $\text{LiCl} + \text{KCl}$ or $\text{NaCl} + \text{KCl}$ salt mix is likely to be significantly contaminated by, in particular, alkali and alkaline earth metal halides. The dissolved contaminants may be removed by ion exchange, for example using a zeolite.

Electrochemical Separation

As an alternative to precipitation to separate out fission products, electrochemical separation may be considered, for example the reduction of lanthanide(III) to lanthanide(0). Electrochemical separation requires a solvent which is not significantly
30 destroyed in the electrowinning process.

Decontamination of Halides Insoluble in the Initial Ionic Liquid Solvent

Halides not dissolved in the chosen ionic liquid may be treated to remove radioactive ions by contacting the undissolved residue with another ionic liquid composition. For example, halides not dissolved in the basic ionic liquid used in the initial dissolution may be treated to remove radioactive ions by contacting the undissolved residue with acidic [emim]Cl-AlCl₃, in which it may be dissolved. The radioactive ions (fission products) may be removed from the resulting solution by, for example, any of the separation techniques mentioned above, especially ion exchange. Acidic [emim]Cl-AlCl₃ is not suitable for dissolving mixtures containing significant NaCl, because this ionic liquid reacts with NaCl to yield neutral, buffered [emim]Cl-AlCl₃ composition which will not dissolve fission product chlorides.

Acidic [emim]Cl-AlCl₃ may be used as solvent in other contexts. Moreover, irrespective of the context, other acidic ionic liquids (e.g. those based on substituted imidazolium and/or containing AlCl₃) may be used in place of [emim]Cl-AlCl₃. Some preferred methods of the invention therefore involve dissolving a metal halide in an acidic ionic liquid.

The cleaned salt composition is then recovered from the ionic liquid and, if required, has its composition adjusted to the eutectic. In one variant, the cleaned salt composition is dissolved in water or another aqueous medium and then extracted with a water-insoluble ionic liquid (e.g. [bmim][PF₆], where [bmim] = 1-butyl-3-methylimidazolium cation). The salt composition may then be re-used.

It will be appreciated, therefore, that the invention includes a method of removing radioactive contaminants from an alkali metal halide composition used in the reprocessing of nuclear fuel, comprising:

- (i) dissolving in an ionic liquid said contaminants to obtain an ionic liquid solution;

(ii) separating said contaminants from the solution by precipitation, solvent extraction or electrochemical reduction;

(iii) then optionally removing contaminants remaining in the solution by ion exchange; and

(iv) recovering the alkali metal halide composition from the solution and, if necessary, adjusting its composition to the eutectic.

10 In some of these methods a residue comprising alkali and/or alkaline earth metal halides remains undissolved in the ionic liquid. The residue is dissolved in an acidic ionic liquid, especially acidic $[\text{emim}]\text{Cl}-\text{AlCl}_3$, to obtain a mixture from which contaminants are removed especially by precipitation or electrochemical reduction and/or by ion exchange.

15 Also included in the invention is the use of an ionic liquid as a solvent for an ionic composition in the selective removal from the dissolved composition of one or more species contained in the composition.

In order that the present invention may be more fully understood, examples will now be given by way of illustration only with reference to the accompanying drawings of which:

Figure 1 is a graph illustrating the effect of changing the composition of AlCl_3 in the ionic liquid $[\text{emim}]\text{Cl}-\text{AlCl}_3$ on LiCl and KCl solubility.

25 Figure 2 is a flowsheet diagram illustrating a process for the extraction of metal chloride from a molten salt mixture using $[\text{emim}]\text{Cl}$;

Figure 3 is a flowsheet diagram illustrating a process for the extraction of metal chloride from a molten salt mixture using concentrated HCl and an $[\text{emim}]\text{Cl}/[\text{omim}]\text{Cl}$ mixture;

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Figure 4 is a flowsheet diagram illustrating a process for the extraction of metal chloride from a molten salt mixture using water and an $[\text{emim}]\text{Cl}/[\text{omim}]\text{Cl}$ mixture;

Figure 5 is a flowsheet diagram illustrating a process for the extraction of metal chloride from a molten salt mixture using methanol and [bmim][BF₄]

- 5 Figure 6 is a flowsheet diagram illustrating a process for the extraction of metal chloride from a molten salt mixture using [bmim][PF₆] and [emim]Cl.

In order to show the effectiveness of the present invention a series of experiments were undertaken in order to determine the maximum amount of individual salts which could be dissolved by [emim]Cl. In these experiments 10g of [emim]Cl was heated to 150° and small quantities (0.5g) of LiCl, KCl and NaCl were added.

The mixture was stirred for a minimum of eight hours or until no solid remained. The results are given in table 1 below which gives the percentage by weight for each salt dissolved in the ionic liquid. The column headed mix refers to a eutectic mixture of LiCl and KCl.

TABLE 1

Chloride	% Weight		
	Run 1	Run 2	Mix
Sodium	0.76	0.74	-
Potassium	0.19	0/17	0.24
Lithium	26.35	25.93	13.78

- 20 It can therefore be seen that LiCl is more soluble in [emim]Cl than KCl or NaCl.

In addition, it has been found that the addition of AlCl₃ to a mixture of LiCl and [emim]Cl results in the precipitation of LiCl. This allows the control of the LiCl solubility by the addition of AlCl₃.

Figure 1 further shows that an increase in the concentration of AlCl_3 in the ionic liquid $[\text{emim}]\text{Cl}$ decreases the solubility of LiCl and in addition, if the concentration of AlCl_3 is further increased, the solubility of KCl increases.

- 5 Referring to Figure 2, the flow sheet schematic diagram 10 shows a process for the removal of metal chloride ionic species in this case gadolinium chloride from a salt mixture. The molten salt mixture of KCl , LiCl and GdCl_3 is placed in a bath 12 and cooled to a solid.
- 10 The solid is removed to a particle size reduction vessel 14 and from there it is combined with the ionic liquid $[\text{emim}]\text{Cl}$ and added to a reaction vessel 18 in which LiCl and GdCl_3 dissolve in $[\text{emim}]\text{Cl}$ and KCl is present as an insoluble solid. The insoluble KCl is removed from reaction vessel 18 to filter 20 where it is filtered, washed and then recycled to the reprocessing plant. LiCl and GdCl_3 are then removed into reaction vessel 22. The
- 15 gadolinium may be removed by electrodeposition and hence extraction from the lithium, or by, for instance, precipitation of a gadolinium phosphate by the addition of a phosphate precursor.

The LiCl can then be removed from the ionic liquid using an organic solvent. The LiCl is

20 then clean and the organic solvent can be removed from the ionic liquid by evaporation and can be sent for re-use at the reprocessing plant. Both the ionic liquid and the molten salt can then be recycled to this extractor process.

Referring to Figure 3, the flow sheet schematic diagram 30 shows a process for the

25 removal of metal chlorides ionic species, in this case gadolinium chloride from a salt mixture. The molten salt mixture comprising KCl , LiCl and GdCl_3 is cooled in a bath 32, the solid mixture is then sent for particle size reduction in the particle size reduction vessel 34. From here the mixture is passed to vessel 38, concentrated HCl 38 being added to dissolve LiCl . As an alternative to the use of HCl , methanol may be used. The

30 resultant LiCl solution is separated from KCl and GdCl_3 by filtration, both being insoluble in concentrated HCl in the separation vessel 38. The LiCl solution is removed to an evaporator 40 where the concentrated HCl is evaporated off and reused. The LiCl is then

washed 42 and can then be sent for recycle in the reprocessing plant. The KCl and GdCl₃ are dissolved in water 46 and a mixture of the ionic liquids [emim]Cl and [omim]Cl are added 50 to the solution 48.

5 The resultant mixture is added to vessel 52 in which the water is evaporated off, causing the formation of a KCl precipitate and leaving GdCl₃ dissolved in the ionic liquid. GdCl₃ is recovered by addition of an organic solvent such as chloroform at 54. The GdCl₃ can thus be filtered off and sent to a further vessel for conversion to oxide. The organic solvent can be removed from the ionic liquid mixture by distillation. The ionic liquid
10 which remains can be recycled in the process by adding at 50. All solvents are thus recycled. LiCl and KCl are now clean and can be returned to the reprocessing plant.

Referring to figure 4, the flow sheet schematic diagram 70 shows a process for the removal of metal chlorides from a salt mixture comprising NaCl, KCl and GdCl₃.

15

The cooled molten salt 72 first passes through a particle reduction step. The salt is then combined with water 74. At this stage any insoluble products are filtered off. To the resultant aqueous solution 76 is added a mixture of the ionic liquids [omim]Cl and [emim]Cl 78. The water is evaporated off from this mixture. The GdCl₃ is soluble in the
20 ionic liquid mixture but the NaCl and KCl are insoluble. As this water is removed, the NaCl and KCl precipitate from the mixture and are passed to vessel 84 for working with an organic solvent. The GdCl₃ is separated from the ionic liquid using an organic solvent such as chloroform. The GdCl₃ is then sent to vessel for oxide conversion, in readiness for vitrification. The organic solvent is removed from the ionic liquid by distillation.
25 Thus both the ionic liquid and the organic solvent can be recycled to the process (point 78 for the ionic liquid). NaCl and KCl can now be recycled to the reprocessing plant.

Referring to figure 5, the flowsheet schematic diagram 90 shows a process for the removal of metal chlorides from a salt mixture comprising NaCl, KCl and GdCl₃. Salt
30 from the molten salt bath 92 is first cooled, then sent for mechanical particle size reduction 94. Methanol 96 is then used as a solvent, dissolving LiCl and GdCl₃ chlorides, but leaving behind KCl in vessel 98. The KCl can be filtered, washed in an organic

solvent 100, and returned to the molten salt bath 92. The $\text{LiCl} / \text{GdCl}_3$ solution is then treated with another ionic liquid such as hot 1-butyl-3-methylimidazolium tetrafluoroborate, $[\text{bmim}][\text{BF}_4]$ (140°C) in vessel 102. The methanol is distilled off 104, and returned to the first dissolution step 96. LiCl will be soluble in the hot $[\text{bmim}][\text{BF}_4]$ whereas GdCl_3 will form a precipitate. The GdCl_3 precipitate can be filtered off 106, sent to oxide conversion, and vitrification.

The LiCl could be precipitated from the $[\text{bmim}][\text{BF}_4]$ by saturation of the solution 108, followed by cooling and filtering off the solid LiCl 110. The $[\text{bmim}]\text{Cl}$ can then be recycled to the process. This process has the advantage that all solvents are thus recycled.

Referring to figure 6, the flowsheet schematic diagram 120 shows a process for the removal of metal chlorides from a salt mixture comprising NaCl , KCl and GdCl_3 . Salt from the molten salt bath 122 is first cooled, then sent for mechanical particle size reduction. The salt particles are then dissolved in an ionic liquid $[\text{bmim}][\text{BF}_4]$ 126 which dissolves LiCl in vessel 128. The remaining solid KCl and GdCl_3 can be filtered off, and sent to the next stage. The LiCl solution in $[\text{bmim}]\text{Cl}$, is then contacted with water or methanol 130, to extract the lithium chloride 132, and the $[\text{bmim}]\text{Cl}$ can be recycled to the process. The KCl and LnCl_3 solids are mixed with an ionic liquid such as $[\text{emim}]\text{Cl}$ 134, into which the GdCl_3 will dissolve 136. The insoluble KCl precipitate can be filtered off, washed and dried and returned to the molten salt bath 138. The gadolinium laden ionic liquid stream, can be thermally decomposed to leave the oxides for vitrification 140.

The method of the present invention may also be used for the extraction of more than one lanthanide salt or other fission products from a eutectic mix. For example, a eutectic mixture comprising 45g LiCl and KCl , 2.5g SmCl_3 and 2.5g GdCl_3 was combined with 45g of methanol or 45g of concentrated hydrochloric acid and stirred for eighteen hours. The sample was then filtered and the resulting solids were collected and dissolved in 50g distilled water. In addition 5g of $[\text{emim}]\text{Cl}$ and 5g of $[\text{omim}]\text{Cl}$ were added to the aqueous solution. The sample was then heated to 100°C for 1 hour and subsequently allowed to cool. 20g of methanol was added and the mixture was filtered, the methanol

was extracted from the resultant liquid to leave a liquid comprised of [emim]Cl, [omim]Cl, SmCl_3 and GdCl_3 .

A similar method was used to extract SmCl_3 and GdCl_3 from KCl and NaCl.

CLAIMS

1. A method of removing from a metal salt ionic species therein, which method comprises contacting the metal salt with an ionic liquid to dissolve the metal salt, the ionic species or both, thereby to form a resultant ionic liquid composition and, at least in the case where both the metal salt and the ionic species are dissolved, said ionic liquid composition is treated to separate the ionic species therefrom and subsequently processed to recover the metal salt.
2. A method of claim 1 wherein the metal salt is one or more alkali metal halides.
3. A method of claim 2 wherein the metal salt is mixture of LiCl and KCl or a mixture of NaCl and KCl.
4. A method of any of claims 1 to 3 wherein the ionic species comprise one or more species selected from cations of the lanthanides, the alkali metals and the alkaline earth metals.
5. A method of Claim 4 wherein the ionic species comprise one or more cations of Sm, Gd, Cs, Ba and Sr.
6. A method of any of Claims 1 to 5 wherein the ionic liquid comprises at least one imidazolium halide, a pyridinium halide or a phosphonium halide, optionally in combination with $AlCl_3$.
7. A method of Claim 6 wherein the ionic liquid is [emim]Cl.
8. A method of Claim 6 wherein the ionic liquid is [emim]Cl in combination with [omim]Cl.
9. A method of Claim 6 which includes the features of claims 3 and 4 and wherein the ionic liquid is basic [emim]Cl- $AlCl_3$ or another basic ionic liquid.

10. A method of Claims 1 to 9 wherein said treatment comprises one or more of salting out, another precipitation method, ion exchange and electrochemical separation.

5 11. A method of Claim 10 wherein the ionic solution contains [LiCl and KCl] or [NaCl and KCl] and at least one lanthanide, and wherein the solution is treated to separate the or each lanthanide therefrom and is subsequently processed to recover the [LiCl and KCl] or [NaCl and KCl], the treatment comprising at least one of the steps of salting out the or each lanthanide as the chloride or chlorides thereof, precipitating out the or each
10 lanthanide as the phosphate or phosphates thereof, or electrochemically separating the or each lanthanide.

12. A method of Claim 10 or Claim 11 wherein the ionic solution further contains alkali and/or alkaline earth metal halides other than [LiCl and KCl] or [NaCl and KCl]
15 and said other halides are removed by ion exchange.

13. A method of any of claims 1 to 12 which comprises dissolving a metal halide in acidic [emim]Cl-AlCl₃ or another acidic ionic liquid.

20 14. A method of claim 12 wherein said metal halide is a residue, insoluble in basic [emim]Cl-AlCl₃, remaining after performing a process of claim 1.

15. A method of Claim 14 wherein the performing of a process of claim 1 involves performing a method of claim 7.

25

16. A method of removing radioactive contaminants from an alkali metal halide composition used in the reprocessing of nuclear fuel, comprising:

- (i) dissolving in an ionic liquid said contaminants to obtain an ionic liquid solution;
- 30 (ii) separating said contaminants from the solution by precipitation or electrochemical reduction;

(iii) then optionally removing contaminants remaining in the solution by ion exchange; and

(iv) recovering the alkali metal halide composition from the solution and, if necessary, adjusting its composition to the eutectic.

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17. A method of Claim 16 wherein the ionic liquid is [emim]Cl or acidic [emim]Cl-AlCl₃.

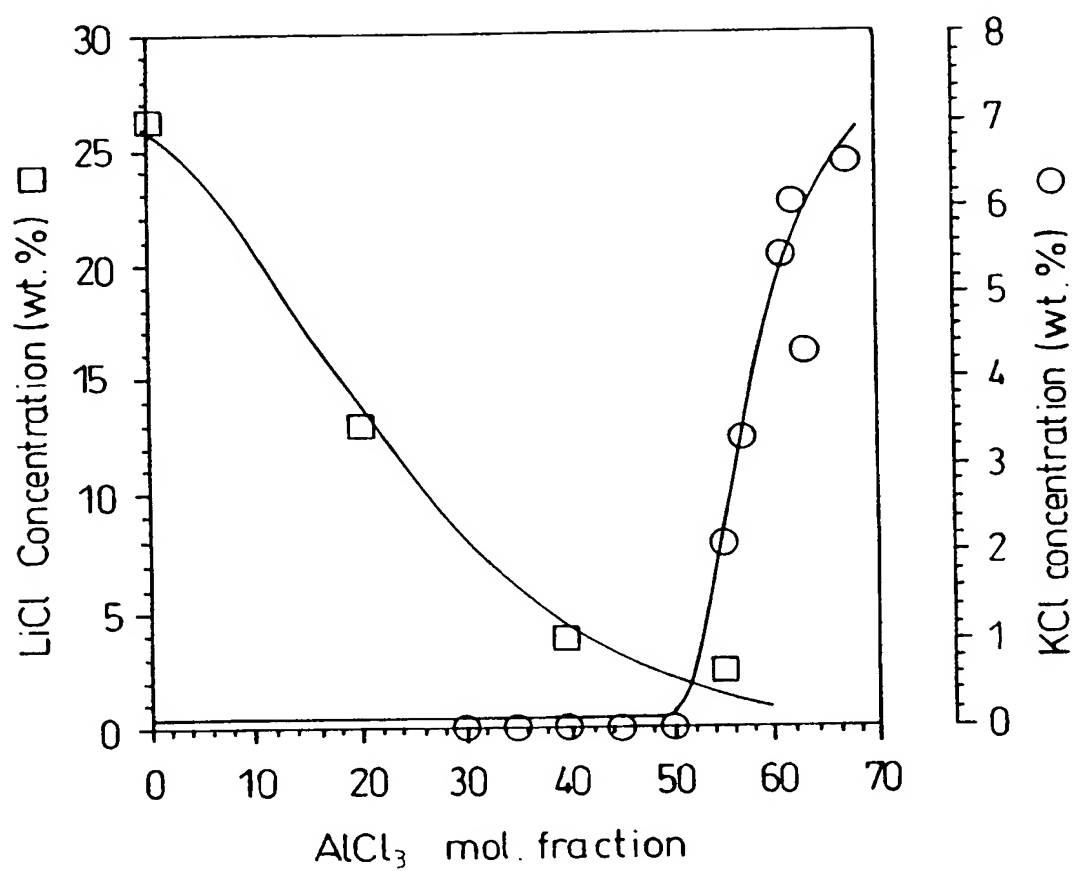
18. A method of Claim 16 or Claim 17 wherein a residue comprising alkali and/or
10 alkaline earth metal halides remains undissolved in the ionic liquid, which residue is dissolved in acidic [emim]Cl-AlCl₃ to obtain a mixture from which contaminants are removed by precipitation or electrochemical reduction and/or by ion exchange.

19. A method of any of Claims 16 to 18, wherein the recovery of the alkali metal
15 halide composition involves its being extracted into an aqueous medium and then extracted into a water-insoluble ionic liquid.

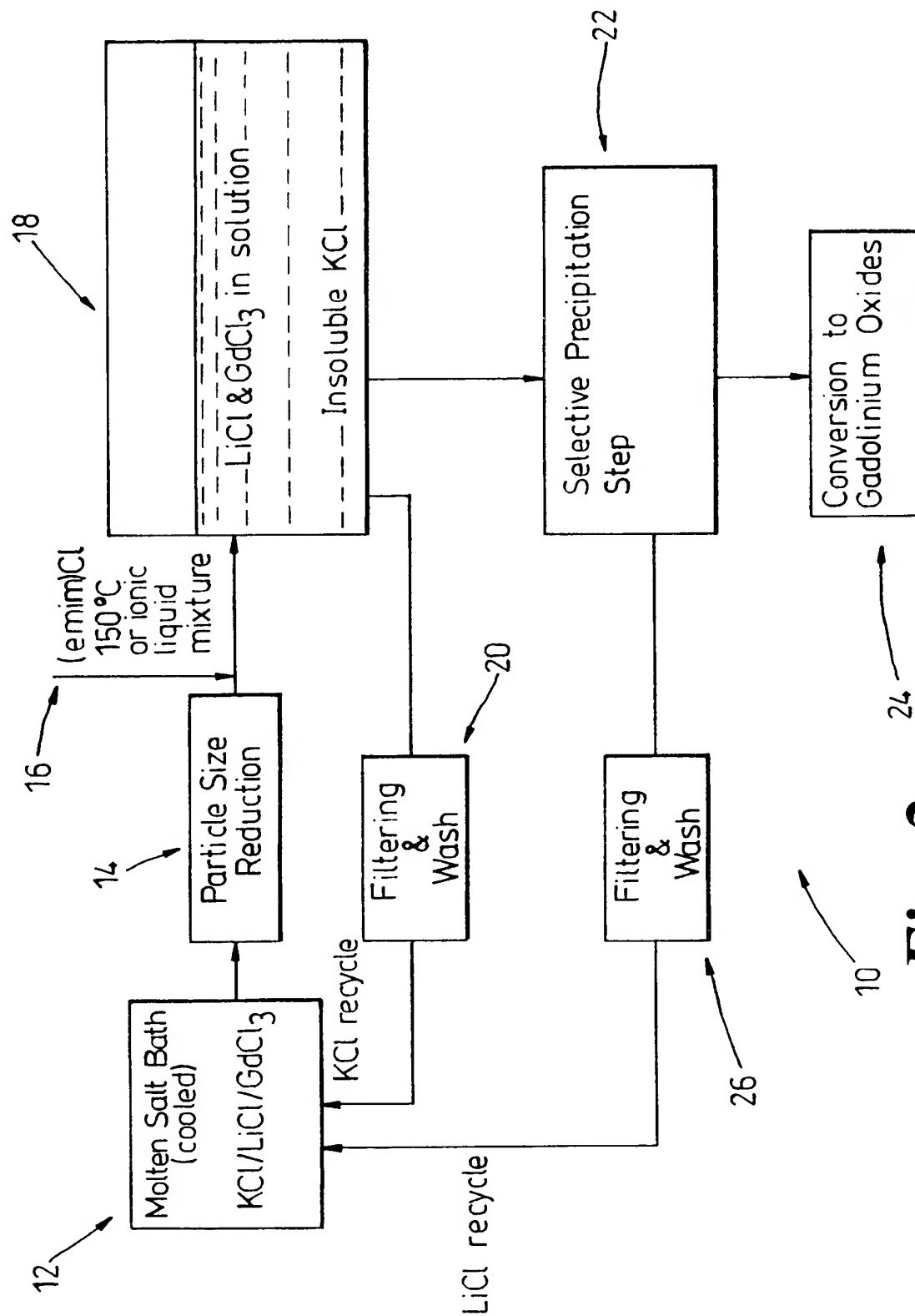
20. A method of any of Claims 16 to 18, wherein the recovery of the alkali metal
20 halide composition involves its being extracted into an aqueous medium followed by addition of a water miscible ionic liquid and removal of the water.

21. The use of an ionic liquid as a solvent in the selective removal from an ionic composition of one or more ionic species contained in the composition.

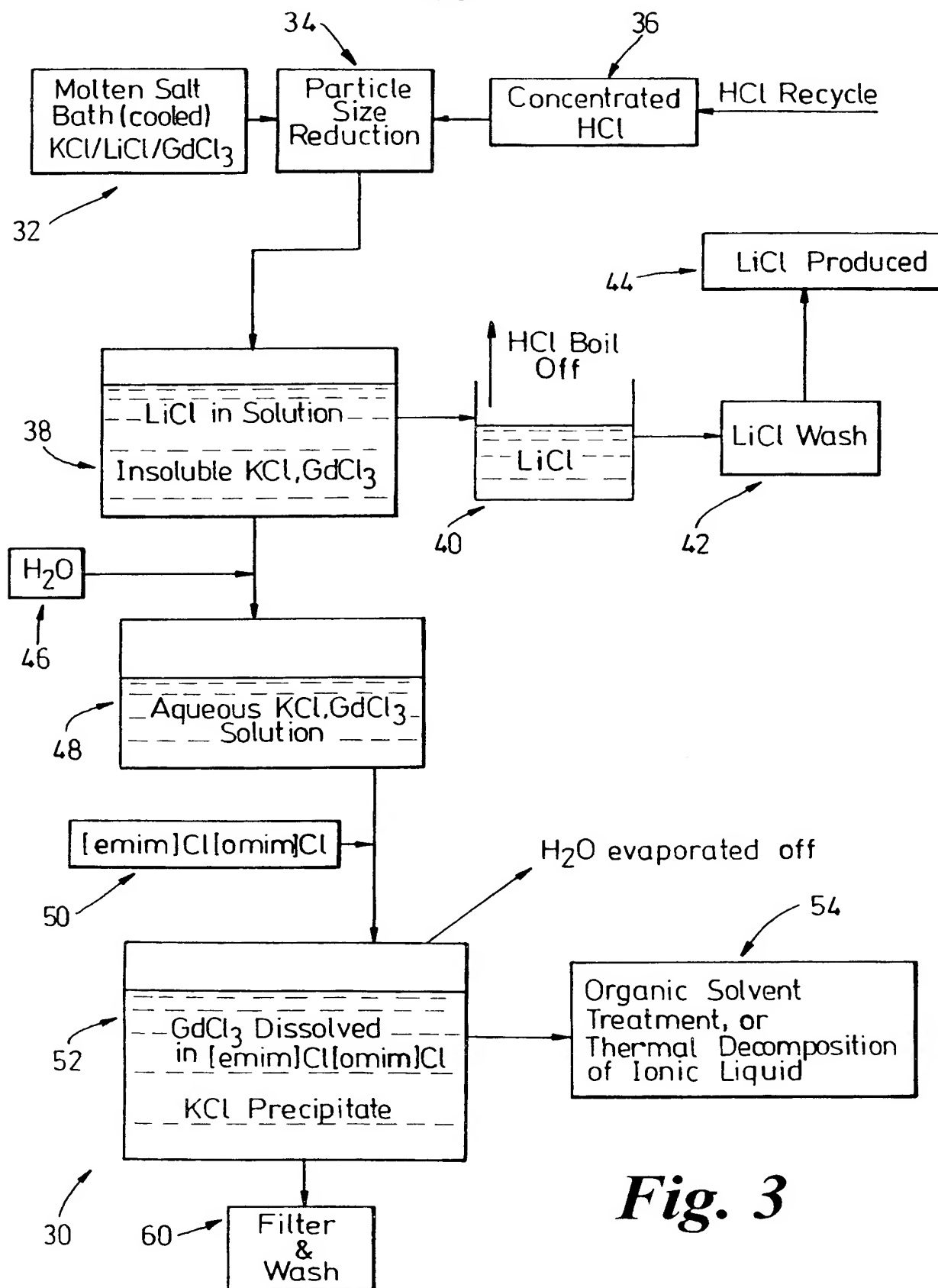
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*Fig. 1*

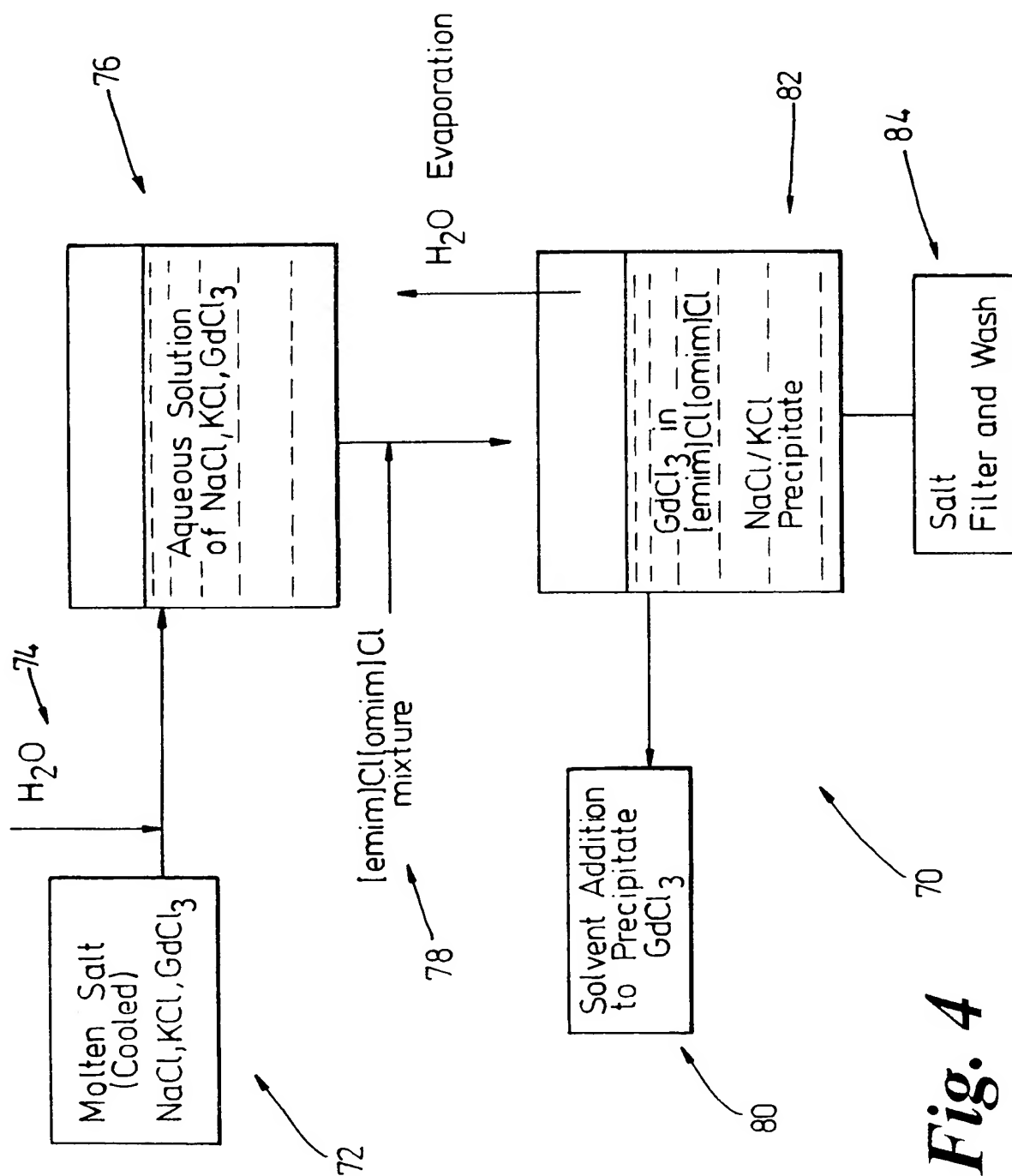
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**Fig. 2**

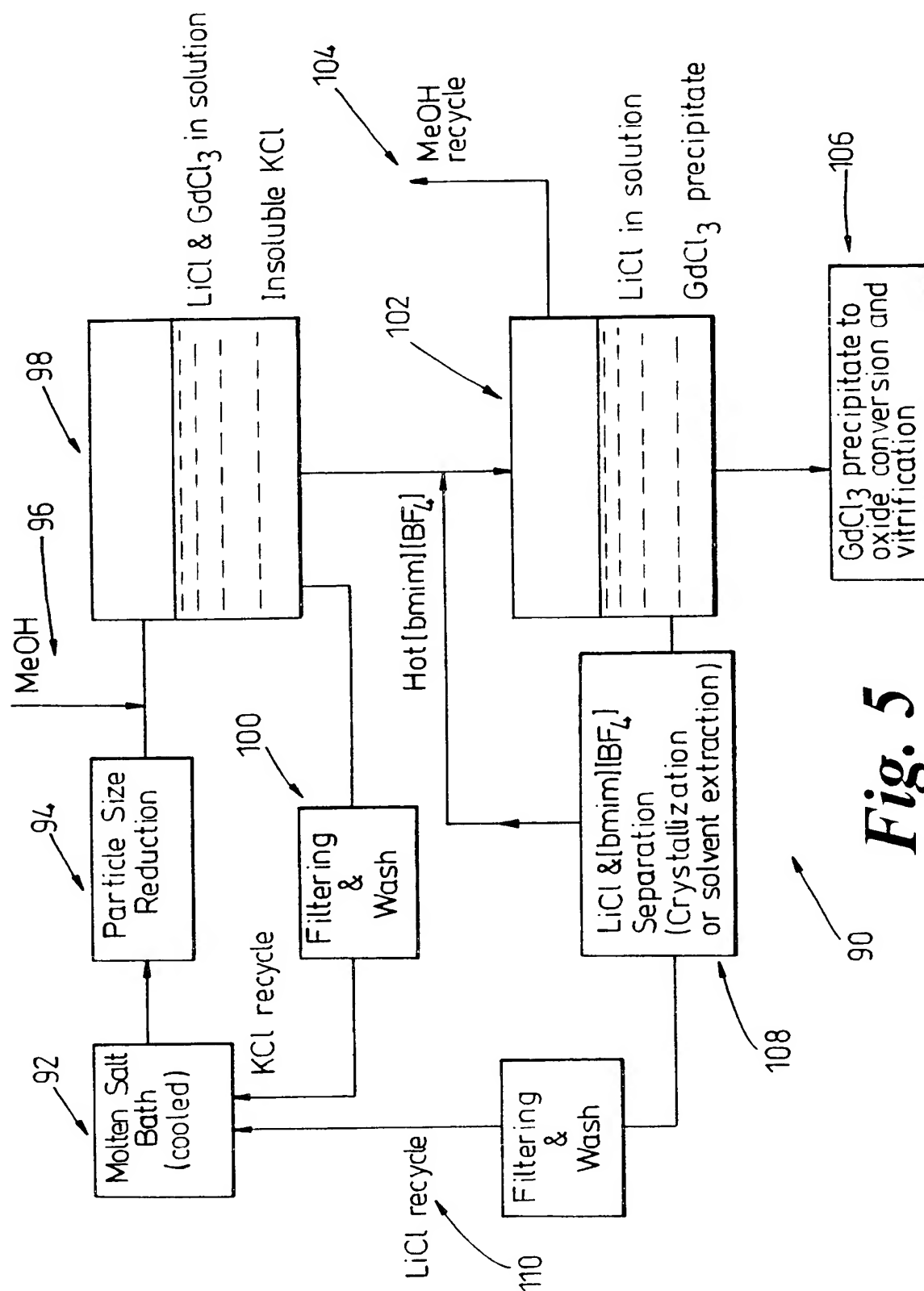
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**Fig. 3**

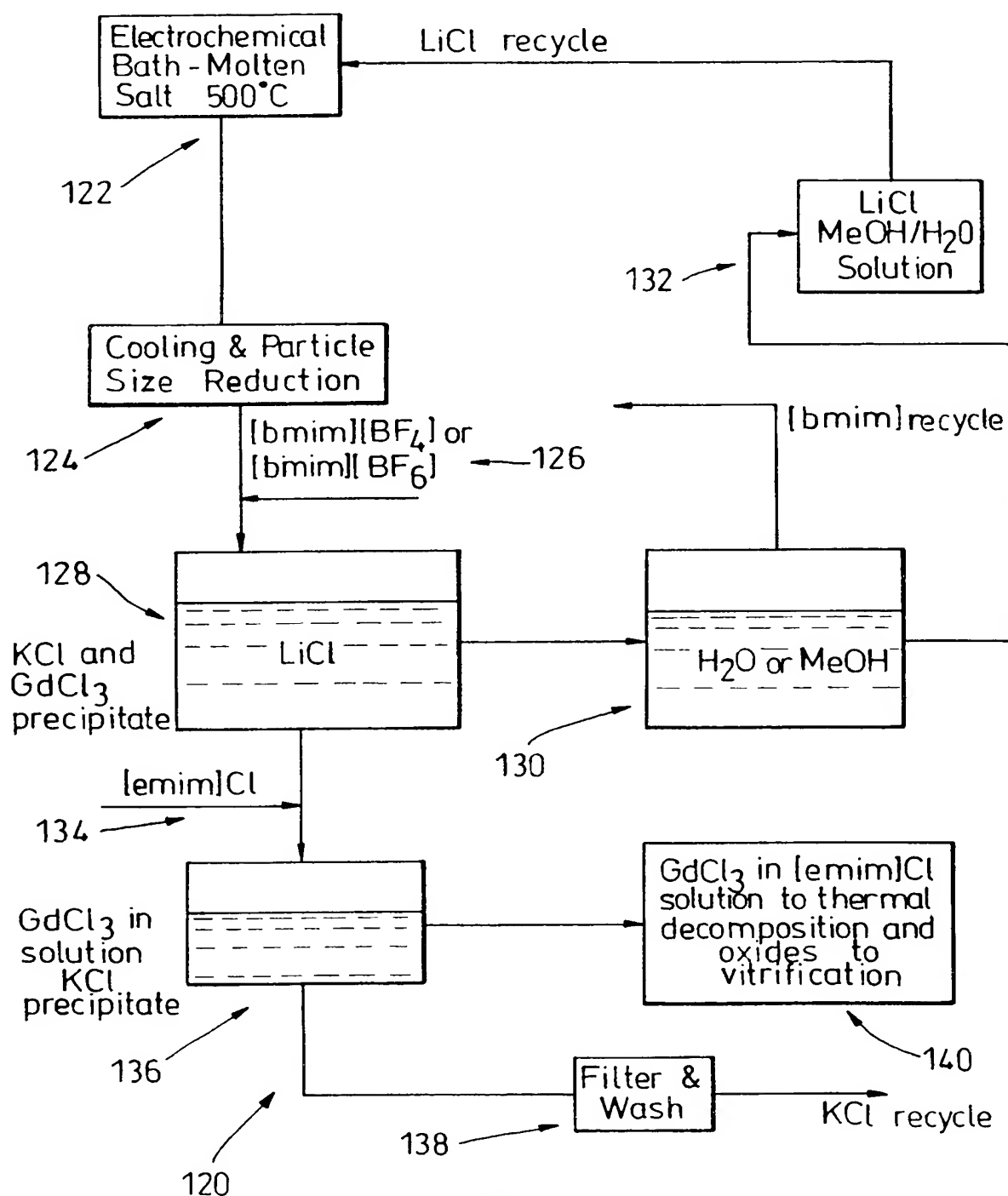
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**Fig. 4**

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**Fig. 5**

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**Fig. 6**

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 98/02743

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C01D3/18 G21C19/48

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
A	SEDDON K R: "IONIC LIQUIDS FOR CLEAN TECHNOLOGY" JOURNAL OF CHEMICAL TECHNOLOGY AND BIOTECHNOLOGY (INTERNATIONAL JOURNAL OF BIOTECHNICAL AND CHEMICAL PROCESSES), vol. 68, no. 4, April 1997, pages 351-356, XP000659374 see the whole document ---	1-21
P, A	WO 98 06106 A (BRITISH NUCLEAR FUELS PLC ; GORDON CHARLES MCINTOSH (GB); FIELDS MA) 12 February 1998 cited in the application see the whole document ---	1-21
A	US 5 336 450 A (ACKERMAN JOHN P ET AL) 9 August 1994 see the whole document -----	1-21

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

*** Special categories of cited documents**

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Shade, M

INTERNATIONAL SEARCH REPORT

Information on patent family members

I. International Application No

PCT/GB 98/02743

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9806106	A	12-02-1998	AU 3703497 A	25-02-1998
US 5336450	A	09-08-1994	NONE	